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EDITOR

N. B. VAUGHAN, M.Sc.

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THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS

ANNUAL GENERAL MEETING

THE FORTY-THIRD ANNUAL GENERAL MEETING of the Institute of Metals was held in London on Tuesday, Wednesday, and Thursday, 13, 14, and 15 March 1951. The meetings on 13 and 14 March were held at the Park Lane Hotel, Piccadilly, W.1; that on 15 March was held at 4 Grosvenor Gardens, S.W.1. The President, Mr. H. S. TASKER, B.A., occupied the Chair at the opening of the meeting.

Tuesday, 13 March

The CHAIRMAN extended a welcome to members and visitors attending the meeting from overseas.

The minutes of the previous General Meeting of the Institute, held in Bournemouth from 18 to 22 September 1950, were taken as read and signed by the Chairman.

ELECTIONS OF ORDINARY MEMBERS, JUNIOR MEMBERS, AND STUDENT MEMBERS

The SECRETARY (Lieut.-Colonel S. C. Guilan, T.D.) announced that, since the last General Meeting, the following 189 Ordinary Members, Junior Members, and Student Members had been elected on 25 September, 30 October, 15 November, and 29 December 1950, and 8 February, 22 February, and 12 March 1951:

ELECTED ON 25 SEPTEMBER 1950

As Ordinary Members

ARMSTRONG, William McColl, B.A.Sc., Associate Professor of Metallurgy, University of British Columbia, Vancouver, B.C., Canada.

BANNER, George James, Metallurgist, The Aston Chain and Hook Co., Ltd., Erdington, Birmingham.

CURRAN, Eugene, O.B.E., Director and General Manager, Curran Steels, Ltd., Cardiff.

DASTUR, Minu N., Sc.D., B.Sc., Chief Metallurgical Engineer, H. A. Brassert and Co., New York, N.Y., U.S.A.

FLINT, Robert Francis, Librarian, Fulmer Research Institute, Ltd., Stoke Poges, Buckinghamshire.

GARDNER, John Frederick, Managing Director, John E. Moore, Ltd., Yeadon, nr. Leeds, Yorkshire.

GEROW, Carlyle, M.B.E., B.Sc., Secretary-Treasurer, The Canadian Institute of Mining and Metallurgy, Montreal, P.Q., Canada.

GIBBS, Leland E., B.S., Manager, Technical Service, Revere Copper and Brass, Inc., Rome, N.Y., U.S.A.

GRUBB, Laurence Charles, B.Sc., Chief Mechanical Engineer, South African Railways, Pretoria, South Africa.

- HOFMANN, Professor Wilhelm, Head, Institut für Werkstoffkunde und Schweisstechnik der Technischen Hochschule, Braunschweig, Germany.
- JONSON, George Ragnar, Assistant Sales Manager, AB Svenska Metallverken, Stockholm, Sweden.
- LADVEZE, Alfred Leon, General Manager, H. J. Maybrey and Co., Ltd., London.
- MCGRADY, Denton Delbert, M.S., Assistant Professor, Metallurgical Engineering Department, Michigan State College, East Lansing, Mich., U.S.A.
- MCGUIRE, Francis Thomas, M.S., Ph.D., Metallurgist, Materials Engineering Department, Deere and Co., Moline, Ill., U.S.A.
- PAINE, Thomas Otten, A.B., M.Sc., Ph.D., Metallurgist, General Electric Co., Research Laboratory, Schenectady, N.Y., U.S.A.
- REID, George Thompson, Technical Adviser, Roberts Castings, Ltd., Holmfirth, nr. Huddersfield, Yorkshire.
- REYNOLDS, Laurence Joseph, Managing Director, L. J. Reynolds and Co., Ltd., Limerick, Eire.
- SIMONETTI, Fiorentini Aurelio, Plant Manager, S.A. Manufacturas de Cobre, Santiago, Chile.
- THOMPSON, Gordon Vallins Elliot, B.Sc., Senior Assistant, Information Department, British Non-Ferrous Metals Research Association, London.

As Student Members

- HINCHLIFFE, Philip Russell, B.Sc., A.M.C.T., In H.M. Forces. (Mail): F.A.U. International Service, Steep, Petersfield, Hampshire.
- JOHN, Vernon Bowen, Student of Metallurgy, University College, Cardiff.
- MORRIS, John, Student of Metallurgy, University College, Cardiff.
- PALCHOUDHURI, Amitaua, B.Sc., Student of Metallurgy, Battersea Polytechnic, London.
- PITTS, David William Norman, B.Sc., Research Student, Sir John Cass Technical Institute, London.

ELECTED ON 30 OCTOBER 1950

As Ordinary Members

- BARRETT, Charles S., B.S., Ph.D., Professor of Metallurgy, University of Chicago, Chicago, Ill., U.S.A.
- BEAUMONT, Frederick William, Works Manager, Wednesbury Tube Company, Ltd., Bilston, Staffordshire.
- CALDERWOOD, W. Hamilton, Technical Representative, Gibbons (Dudley), Ltd., Dudley, Worcestershire.
- COLES, Graham Winton, B.Sc., Metallurgist, Stewarts and Lloyds, Ltd., Corby, Northamptonshire.
- COOK, Albert Rundle, B.A., Metallurgist, Almag Engineering Company, Ltd., Liverpool.
- GUTTENSTEIN, Konrad, Managing Director, Loewy Engineering Company, Ltd., Bournemouth, Hampshire.
- HAFFNER, Eduard K. L., Director and Chief Engineer, Loewy Engineering Company, Ltd., Bournemouth, Hampshire.
- LAHURI, Colonel Birendra Nath, M.Sc., Ph.D., Ordnance Consulting Officer for India, London.
- MOELLER, Roger David, M.S., Metallurgist, Los Alamos Scientific Laboratory, Los Alamos, N.M., U.S.A.
- MOORBY, Frederick Herbert, Radiologist and Metallurgist, John Dale, Ltd., London Colney, Hertfordshire.
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- PAGE, Edward John, Foundry Supervisor, Copper and Alloys, Ltd., West Bromwich, Staffordshire.
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- SIMS, Clarence Edgar, M.Sc., Research Metallurgist, Battelle Memorial Institute, Columbus 1, O., U.S.A.
- WEITLAUF, Frederica M., Technical Librarian, Timken Roller Bearing Company, Canton, O., U.S.A.
- WILLIAMS, Caleb George, Metallurgist, Norton Motors, Ltd., Birmingham.

As Junior Member

- STEWART, Robert Graham, B.Met.E., Metallurgist, Materials Engineering Department, Commonwealth Aircraft Corporation Pty., Ltd., Port Melbourne, Australia.

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- GRIMWOOD, Kenneth William, Assistant Metallurgist, Enfield Rolling Mills, Ltd., Brimsdown, Enfield, Middlesex.
- HALL, Brian William, Laboratory Assistant, George Morgan, Ltd., Birmingham.
- HOOPER, Frank Arthur, Assistant Metallurgist, George Morgan, Ltd., Birmingham.
- MOHAN, Anand, M.Sc., Research Student, Department of Metallurgy, Indian Institute of Science, Bangalore, India.
- WRIGHT, Colin Bernard, B.A., Research Student, Royal Institution, London.

ELECTED 15 NOVEMBER 1950

As Ordinary Members

- BOUCHARD, Jean, Consulting Engineer, Issy-les-Moulineaux (Seine), France.
- BÜCKLE, Helmut, Dr.-Ing., Metallurgist, Office National d'Etudes et Recherches Aéronautiques, Paris, France.
- DUNKLEY, Christopher Charles, B.Sc., Works Engineer, James Bridge Copper Works, Ltd., Walsall, Staffordshire.
- EFJESTAD, Dagfin, Works Manager, A/S Årdal Verk, Årdalstangen i Sogn, Norway.
- HAMILTON, Alan William, Representative, Imperial Chemical Industries, Ltd., Metals Division, Glasgow.
- JACOBSON, Francis S., Metallurgical Engineer, Kaiser Steel Corporation, Fontana, Calif., U.S.A.
- LANGEN, Mathias, Director and Chief Engineer, Loewy Engineering Company, Ltd., Bournemouth, Hampshire.
- POTEMKINE, Wladimir, Office National d'Etudes et Recherches Aéronautiques, Châtillon/Bougneux (Seine), France.
- THOMAS, Charles Shenton, Inspecting Engineer, Rendel, Palmer and Tritton, London.
- WORMWELL, Frank, M.Sc., Ph.D., Research Chemist, Chemical Research Laboratory, Teddington, Middlesex.

As Student Members

- ALLMAND, Thomas R., Student of Metallurgy, Battersea Polytechnic, London.
- BRITTON, John, Student of Metallurgy, University College, Swansea.
- CAPUS, Joseph Michael, Student of Metallurgy, University of Birmingham.
- CHANGARNIER, Christiane, Office National d'Etudes et Recherches Aéronautiques, Paris, France.

- COX, Antony Hugh, Student Metallurgist, John Dale, Ltd., London Colney.
 DODD, John, Student of Metallurgy, King's College, Newcastle-on-Tyne.
 HILL, Sidney James Thomas, Student of Metallurgy, Johnson, Matthey and Co., Ltd., London.
 JACKSON, Norman Henderson, Student of Metallurgy, King's College, Newcastle-on-Tyne.
 JAMES, Brian Patterson, Student of Metallurgy, Sheffield University.
 MILLS, Stuart Edward, Student of Metallurgy, Sheffield University.
 MORTON, Alan, Student of Metallurgy, Sheffield University.
 PROUDFOOT, Edward, Student of Metallurgy, King's College, Newcastle-on-Tyne.
 WILLIAMS, Edward, Metallurgical Assistant, North Thames Gas Board, Watson House Laboratories, London.
 YORKE, Joan Margaret, Student of Metallurgy, Battersea Polytechnic, London.

ELECTED 29 DECEMBER 1950

As Ordinary Members

- BOURNE, Leonard, B.Met., Metallurgist, The British Iron and Steel Research Association, Sheffield.
 BROWN, Tom, Director, The Sheepbridge Company, Ltd., Chesterfield, Derbyshire.
 COBB, Keith Loveland, Managing Director, H. J. Enthoven and Sons, Ltd., London.
 FREEMAN, J. W., B.S., M.S.E., Ph.D., Associate Professor and Research Engineer, Engineering Research Institute, University of Michigan, Ann Arbor, Mich., U.S.A.
 HAFSTAD, Magne, Works Manager, AB Svenska Aluminiumkompaniet, Sundsvall, Sweden.
 MAKOW, Victor Georges, Dr.-Ing., Consulting Engineer, Madrid, Spain.
 MILLER-HALLETT, George, B.A., Partner, Hallett and Son, London.
 MOUDGILL, J. N., B.A., B.Sc., Officiating Professor, Department of Mechanical Engineering, University of Roorkee, Roorkee (U.P.), India.
 PATERSON, Kenneth, A.M.C.T., Director, Park and Paterson (Manchester), Ltd., Marple, Cheshire.
 PINTO, Norman P., S.B., Senior Engineer, Sylvania Electric Products, Inc., Bayside, Long Island, N.Y., U.S.A.
 SCHWARZ, Hanns, Managing Director, Rau-Metallwerk-Gesellschaft, München, Germany.
 SHALER, Amos Johnson, D.Sc., Scientific Liaison Officer, Office of Naval Research, United States Embassy, London.
 SMITH, Richard Fox, Mechanical Engineering Inspector, "Savages", Mizen Way, Cobham, Surrey.

As Junior Members

- HEATH, Alfred Russell, B.Sc., Bursar, British Non-Ferrous Metals Research Association, London.
 HUNT, James Bernard, A.M.C.T., Metallurgist, Bahrein Petroleum Company, Ltd., Awali, Bahrein Island, Persian Gulf.
 LANGFORD, Sydney Reginald Arthur, Research Metallurgist, James Booth and Co., Ltd., Birmingham.
 THACKRAY, Frederick Kenneth, Assistant Metallurgist, McKechnie Brothers, Ltd., Birmingham.

As Student Members

- BADER, Michael Geoffrey, Apprentice Metallurgist, de Havilland Aircraft Company, Ltd., Hatfield, Hertfordshire.

BOOTHE, James Albert, Student of Metallurgy, Toronto University, Canada.
BUCKLOW, Ian Alfred, B.A., Student of Metallurgy, Cambridge University.
CAMPBELL, Graeme Havelock, Student of Metallurgy, Cambridge University.
CAWTHORNE, Clifford, Student of Metallurgy, Sheffield University.
COLE, Michael, Student of Metallurgy, Cambridge University.
EDGE, Arthur Moore, Student of Metallurgy, Sheffield University.
HAINS, Jack Whitby, B.A., Student of Metallurgy, Cambridge University.
HOLLINGBERRY, Desmond Robert, Student of Metallurgical Engineering, University of Toronto, Canada.
HUTCHISON, Peter, Laboratory Assistant, The Mond Nickel Co., Ltd., Development and Research Department, Birmingham.
MARTIN, John Wilson, B.A., Student of Metallurgy, Cambridge University.
MORGAN, William Austin, B.Sc., Research Student, Cambridge University.
MORTIMER, Ian Grant, Student of Metallurgy, Cambridge University.
ROWE, William Moseley, Student of Metallurgy, University College, Cardiff.
SHAKESPEARE, Alan Gough, B.A., Student of Metallurgy, Cambridge University.
THOMAS, Gareth, Student of Metallurgy, University College, Cardiff.
WEST, John, Student Naval Architect, Hebburn, Co. Durham.
WILCOCK, Jack, Student of Metallurgy, Liverpool University.

ELECTED 8 FEBRUARY 1951

As Ordinary Members

BERGER, Michael Montague, Chairman and Managing Director, Wilkes Berger Engineering Company, Ltd., London.
CHALMERS, James Lauder, M.B.E., M.C., Managing Director, E. Chalmers and Company, Ltd., Leith, Edinburgh.
FELIX, Werner A., Dipl. Ing., Chief of the Materials Testing Laboratory, Gebr. Sulzer A. G., Winterthur, Switzerland.
FINNISTON, Harold Montague, B.Sc., Ph.D., A.R.T.C., Chief Metallurgist, Atomic Energy Research Establishment, Harwell, Berkshire.
FRATER, Edward Charles, Secretary, Loewy Engineering Company, Ltd., Bournemouth, Hampshire.
HAYWOOD, R. A., Research Metallurgist, Universal Grinding Wheel Company, Ltd., Stafford.
JEWELL, Ronald Colgan, B.Sc., A.R.S.M., Director and Chief Metallurgist, Sheffield Smelting Company, Ltd., Sheffield.
PATON, Charles Peter, B.Eng., General Works Manager, Northern Aluminium Company, Ltd., London.
RICHARDS, Lynn Griffith, B.S., Research Technician, Metallurgy Laboratory, Johns Hopkins University, Baltimore, Md., U.S.A.
ROMER-LEE, Knyvett, M.A., Senior Executive Assistant, British Non-Ferrous Metals Federation, Birmingham.
SHIELDS, Harry Gordon, Director, E. Chalmers and Company Ltd., Leith, Edinburgh.
SUTTON, Charles Thomas William, M.Sc., Associate Director and Chief Cable Engineer, Enfield Cables, Ltd., Brimsdown, Middlesex.
TABARY, (Mlle.) Andrée, Ingénieur Sous-chef du Service Recherches et Laboratoires, Compagnie de Fives-Lille, Lille (Nord), France.
WOOD, Dennis, Assistant Works Manager, Charles Clifford and Son, Ltd., Birmingham.
YOUNG, R. F. S., General Manager, Non-Ferrous Tube Company (Pty), Ltd., Springs, Transvaal, South Africa.

As Student Members

- ALMOND, John Kenneth, Student of Metallurgy, Royal School of Mines, London.
- ATKINSON, Charles Edward, Trainee, W. G. Jenkinson, Ltd., Sheffield 1.
- BARLEGGs, Roy Ernest, Student of Metallurgy, Royal School of Mines, London.
- BARRY, Beresford Thomas Kingcome, Student of Metallurgy, Royal School of Mines, London.
- BRIDGES, Dennis Francis, Student Metallurgist, Southern Forge, Ltd., Langley, Buckinghamshire.
- CATTERALL, Graham John, Student of Metallurgy, Royal School of Mines, London.
- CHANDLER, Kenneth A., Student of Metallurgy, Royal School of Mines, London.
- CLOW, Colin George, Student of Metallurgy, Royal School of Mines, London.
- EASTEAL, Charles Dennis, Student of Metallurgy, Royal School of Mines, London.
- FLATLEY, Peter, Student of Metallurgy, Royal School of Mines, London.
- FULWELL, Michael David, Student of Metallurgy, Royal School of Mines, London.
- GREEN, Edward Charles, Student of Metallurgy, Royal School of Mines, London.
- KESSLER, Sebastian W., B.S., Student of Metallurgy, Johns Hopkins University, Baltimore, Md., U.S.A.
- KNOWLES, David Ross, B.Sc., Physicist, Magnesium Elektron, Ltd., Manchester.
- McKECHNIE, Alec R., Student of Metallurgy, Royal School of Mines, London.
- PATRICK, Alan Walters, Student of Metallurgy, Royal School of Mines, London.
- PEARCE, Richard Gerald Anthony, Student of Metallurgy, Royal School of Mines, London.

ELECTED 22 FEBRUARY 1951

As Ordinary Members

- BUNCE, Ronald Gordon, Metallurgist, Pirelli General Cable Works, Ltd., Eastleigh, Hampshire.
- CAREY, Edward Samuel, B.Met., Metallurgist, Mellowes and Co., Ltd., Sheffield.
- CARLSON, Theodore H., B.Eng., Assistant Plant Metallurgist, Bridgeport Brass Company, Indianapolis, Ind., U.S.A.
- CLEAVES, Harold E., B.S., Metallurgy Division, National Bureau of Standards, Washington, D.C., U.S.A.
- EDMAN, Ernest Erik Teodor, Engineer, Telefon AB.L.M. Ericsson, Stockholm, Sweden.
- FISHER, John S., E.E., President, General Metals Powder Company, Akron, O., U.S.A.
- GRIFFITHS, Sidney Howard, Metallurgist and Research Engineer, John Thompson, Ltd., Wolverhampton.
- HASTINGS, Wallace H., Superintendent, Chicago Extruded Metals Company, Cicero, Ill., U.S.A.
- HELLBOM, Kjell Bertil, Metallurgist, Söderfors Steel Works, Söderfors, Sweden.
- MAMET, Charles Jean Valérie Ad le, Directeur-Gérant, S.A. de Construction des Appareils pour L'Industrie, Vilvorde, Belgium.
- MILLER, Frank C., Vice-President, Chicago Extruded Metals Company, Cicero, Ill., U.S.A.

MORRIS, Cecil Edward, Chief Chemist, Universal Metal Products, Ltd., Salford, Lancashire.

ROCCA, Roberto, D.Sc., Consulting Engineer, Techint, Milan, Italy.

As Junior Member

JOHNSTONE, Samuel Thomas Murray, B.Met.E., Scientist, Department of Supply, Melbourne, Vic., Australia.

As Student Members

DOYLE, Nicholas Edward, B.S., Research Assistant, Rensselaer Polytechnic Institute, Troy, N.Y., U.S.A.

DUCKFIELD, Baden John, Student of Metallurgy, University College, Swansea.

EATON, Norman Frank, Student of Metallurgy, University College, Swansea.

EDWARDS, Derek, Student of Metallurgy, University College, Swansea.

HINETT, Oliver John, Electrical Testing Laboratory, J. Sankey and Sons, Ltd., Wolverhampton.

LOCKYER, Edward Brian, Student of Metallurgy, College of Technology, Manchester.

MCPHERSON, Donald Lloyd, Student of Metallurgy, University of Toronto, Canada.

RUCKMAN, James Christopher, Assistant Experimental Officer, Atomic Energy Research Establishment, Harwell, Berkshire.

VICKERS, Harold, Student of Metallurgy, King's College, Newcastle-on-Tyne.

WILLIAMS, Neville Thomas, Student of Metallurgy, University College, Swansea.

ELECTED 12 MARCH 1951

As Ordinary Members

BAER, Alfred Max, Rickling House, Quendon, Saffron Walden, Essex.

BLACKWELL, Peter Alan, B.Sc., Metallurgist, Wild-Barfield Electric Furnaces, Ltd., Watford, Hertfordshire.

BRONCKART, Jérôme Richard, Managing Director, Marcinelle, Belgium.

CAVALLARO, Professor Leo, Dean of the Faculty of Mathematical, Physical, and Natural Sciences, and Director, Chemical Institute, University of Ferrara, Italy.

CLARKE, Major William, J.P., Chief Inspector, Aero Zipp Fasteners, Ltd., Pontypridd, Glamorganshire.

EVANS, Noel Hugh, Deputy Chief Inspector, Richard Thomas and Baldwins, Ltd., Light Alloy and Fabricating Section, Briton Ferry, Glamorganshire.

FRASER, Oliver B. J., B.Sc., Assistant Manager, Development and Research Division, The International Nickel Company, Inc., New York, N.Y., U.S.A.

GEERAERTS, Victor Emmanuel, Manager, Fonderie Geeraerts, Anderlecht, Bruxelles, Belgium.

KNIGHT, Harry Jack, Chief Industrial Engineer, Shell-Mex and British Petroleum, Ltd., Lubricants Department, London.

LAMBOT, Honoré, Dr.es.Sci., Chef de Travaux, Institut de Cristallographie, Université de Liège, Belgium.

LLOYD-LUCAS, Ernest, Managing Director, E. Silver (Bond Street), Ltd., London.

MCDONNELL, John Gabriel, B.Sc.(Eng.), Assistant Sales Manager, Morgan Crucible Company, Ltd., London.

MAGNIETTE, Gaston, General Manager, Société Franco-Belge des Laminoirs et Tréfileries d'Anvers "LAMITREF", Société Anonyme, Anvers, Belgium.

- MAYO, Reginald George P., Technical Engineer, Impregnated Diamond Products, Ltd., Gloucester.
- MITCHELL, Evan J. K., Chief Metallurgist and Foundry Manager, Renfrew Foundries, Ltd., Hillington, Glasgow.
- DE ROSÉE, Baron Frédéric, Administrateur-Directeur, Société des Usines à Cuivre de Moulins, pas Yvois, Belgium.
- STEVENS, Edward Owen, Technical Assistant to the Works Manager, Chemistry and Metallurgy, S. and R. J. Everett and Company, Ltd., Thornton Heath, Surrey.
- WILLIS, Raymond, Works Director, Darwin's Ltd., Sheffield.

As Student Members

- BERRY, John Trevor, Student of Metallurgy, University of Birmingham.
- BROOKES, Kenneth J. A., Laboratory Assistant, British Non-Ferrous Metals Research Association, London.
- CRYSTAL, Harold, Student of Metallurgy, College of Technology, Manchester.
- DAVIES, Bernard Leonard, Student of Metallurgy, College of Technology, Manchester.
- LIDDELL, Frank Robert, Student of Metallurgy, College of Technology, Birmingham.
- MARSDEN, Brian William Hugh, Student of Metallurgy, University College, Swansea.
- MARSDEN, Terence Barclay, Student of Metallurgy, University College, Swansea.
- MORRIS, Kenneth Arthur, Metallurgical Apprentice, Stewarts and Lloyds, Ltd., Bilston, Staffordshire.
- PRESTT, John Stewart, Student of Metallurgy, College of Technology, Manchester.
- SIMPSON, Rex, Student of Metallurgy, University of Manchester, Manchester.

REPORT OF COUNCIL

The CHAIRMAN (Mr. H. S. Tasker, B.A.) in formally moving the adoption of the Report of Council for the Year Ended 31 December 1950, which is printed on pp. 667-676 of this volume, said that, up to the date of the meeting, an appeal which had been made to the non-ferrous metallurgical industries for regular financial support of the Institute's work had resulted in the receipt, under covenant for a period of not less than 7 years, of an annual income of £4867, and that a number of companies in Great Britain and abroad had promised annual subscriptions (not under covenant) amounting to £1911. In addition, donations, which might or might not be repeated, totalled £1200. He thought that these results were very gratifying, and expressed the thanks of the Institute to the generous subscribers and donors of these sums, which would enable the Institute to maintain and develop its work and the Council to be freed from undue financial anxiety in the next seven years.

Mr. A. R. POWELL (Member of Council) seconded the motion, which was carried without dissent.

REPORT OF THE HONORARY TREASURER

The HONORARY TREASURER (Mr. W. A. C. Newman, O.B.E.) presented his Report and the Accounts for the Financial Year Ended 30 June 1950, which are printed on pp. 677-684 of this volume, and moved their adoption.

The accounts followed, in general, the pattern of the last few years—an expanding and progressive Institute whose income had not been able to follow in step. There were few changes in the Balance Sheet. On the liabilities

side, as compared with the previous year the current surpluses were down by £1400. Current liabilities had increased by £300 and Special Funds by £370. On the assets side, the fixed assets had increased slightly, while the total of investment and funds had diminished by £800 and current assets by £300.

The income during the year had been less than the expenditure by £1497, against £864 in the previous year. The deficiency had been met by a transfer from the War-time Emergency Fund, which had now been reduced (during the preceding five years) to about 27% of its original total.

Leaving apart any expenditure on, or income from, Special Publications, there had been a deficiency of income in each of the previous few years of approximately £2000. This figure was still tending to increase and the end of the upward trend was not in sight—costs, staff, issues of *Journal*, and postage, had all been larger and dearer. The War-time Emergency Fund had served a good purpose in meeting these increasing demands so far, but at the current rate of withdrawals it would soon run out. The general appeal instituted by the President was only just in time to prevent the development of a gap in the Institute's finances which could not easily be bridged from current resources—otherwise than by calling on capital.

As an indication, the estimates for 1950–1951 (and such estimates were normally found to be very close) showed that, omitting again expenditure on, and income from, Special Publications, the probable excess of expenditure this year would be of the order of £4000. The estimate of a desirable increase in income of £5000 per annum would not, therefore, be too great.

With the success of the President's appeal in mind, it was probably unfair to introduce any remarks in a minor key. Two points covering the appeal occurred to him, however.

(1) The increase in funds had been mostly by way of covenants over a period of seven years. This period was thus a respite during which the advancement of the Institute and its financial basis could be thoroughly explored, so that the future might be confidently assured. At the end of the seven years it was safe to say that relative expenditure would not have diminished, and that the importance and need of the Institute would have increased. Great as the present success was, the ultimate problem of financing it still remained to be solved.

(2) The acquisition of the new funds imposed an additional trust and responsibility on the Council, its Officers, and its Staff to apply them wisely and economically in the interests of the members. That responsibility was accepted very seriously.

Those who formed the Institute some 43 years ago could not have foreseen the development being witnessed today. Those who enjoyed the present-day privileges and advantages might well wonder what would have happened, and where the voluminous researches of these days would have been recorded for the benefit of the non-ferrous industry as a whole, if there had been no Institute of Metals.

The fact that there was such a body thriving and in good shape, now equipped for a period with additional funds by, he trusted, a grateful and appreciative industry, emboldened him to hope that the relationship between industry and ourselves would become ever closer to the advantage of both.

Major C. J. P. BALL, D.S.O., M.C. (Vice-President and Chairman of the Finance and General Purposes Committee), seconded the motion, which was carried without dissent.

RE-ELECTION OF AUDITORS

It was proposed, seconded, and carried unanimously that Messrs. Poppleton and Appleby be re-elected auditors to the Institute for the ensuing year.

ELECTION OF OFFICERS FOR 1951-52

The SECRETARY announced that the following officers had been elected to fill vacancies on the Council for the year 1951-52 :

President :

Professor A. J. MURPHY, M.Sc.

Vice-Presidents :

A. B. GRAHAM

P. V. HUNTER, C.B.E.

Ordinary Members of Council :

K. W. CLARKE

CHRISTOPHER SMITH

The Secretary also announced that Mr. H. F. SHERBORNE, M.C., M.A., who had been elected an Ordinary Member of Council, had, since election, withdrawn owing to pressure of business. In consequence, the Council had, under the powers granted to it in Article 28, elected Mr. ALFRED BAER to fill the vacancy, and Mr. Baer would present himself for re-election at the next Annual General Meeting.

SENIOR VICE-PRESIDENT

The SECRETARY announced that the Council had elected Dr. C. J. SMITHELLS, M.C., to be Senior Vice-President for 1951-52, and that he would be its next nominee for the Presidency.

INSTITUTE OF METALS (PLATINUM) MEDAL

The CHAIRMAN announced that the Institute of Metals (Platinum) Medal for 1951 had been awarded to Dr. R. W. DIAMOND, Vice-President and General Manager of The Consolidated Mining and Smelting Company of Canada, Ltd., in recognition of his outstanding services to the non-ferrous metallurgical industries in connection with his researches on differential flotation, as applied to the complex Sullivan ore, and as manager of the largest combined lead and zinc producer in the world.

W. H. A. ROBERTSON MEDAL

The CHAIRMAN announced that the W. H. A. Robertson Medal had been awarded to Mr. CHRISTOPHER SMITH, for his paper on "The Extrusion of Aluminium Alloys" (*Journal*, 1949-50, vol. 76, pp. 429-451).

ROSENHAIN MEDAL

The CHAIRMAN announced that the first award of the Rosenhain Medal had been made to Professor G. V. RAYNOR, D.Sc., D.Phil., M.A., for his outstanding contributions in the field of physical metallurgy, in connection with our knowledge of the constitution and formation of alloys.

VOTE OF THANKS TO RETIRING OFFICERS

The CHAIRMAN proposed, and there was carried with acclamation, a hearty vote of thanks to the following retiring officers for their services on the Council: Sir William Griffiths, D.Sc. (Past-President), Dr. S. F. Dorey, C.B.E., Wh.Ex., F.R.S. (Vice-President), and Mr. John Arnott, Dr. Maurice Cook, and Mr. D. P. C. Neave, M.A. (Ordinary Members of Council).

INDUCTION OF THE NEW PRESIDENT

The CHAIRMAN (Mr. H. S. Tasker, B.A.) then introduced the new President, Professor A. J. MURPHY, M.Sc., and inducted him into the Chair.

The PRESIDENT (Professor A. J. Murphy, M.Sc.) briefly thanked the members for the honour of election to the Presidency.

VOTE OF THANKS TO THE RETIRING PRESIDENT

Dr. C. J. SMITHELLS, M.C. (Senior Vice-President), in proposing a very hearty vote of thanks to Mr. H. S. Tasker for his services to the Institute as President, said that Mr. Tasker was an industrialist who had always recognized the importance of fundamental research to industry and, in a sense, he had given effect to this recognition in his very successful appeal to industry for financial support of the work of the Institute. He had rendered great services to the Institute in many directions, and in particular in the field of metallurgical education.

Professor H. O'NEILL, D.Sc., M.Met. (Vice-President), seconded the motion, which was put to the meeting and carried with acclamation.

Mr. TASKER briefly responded.

PRESIDENTIAL ADDRESS

The President, Professor A. J. MURPHY, M.Sc., then delivered his Presidential Address, which is printed on pp. 117-128 of the *Journal*, 1951, vol. 79.

A vote of thanks to the President for his Address was proposed by Mr. E. H. JONES (Member of Council), seconded by Mr. G. L. BAILEY, M.Sc. (Member of Council), and carried with acclamation.

The meeting then adjourned.

LUNCHEON

A luncheon was held at the Park Lane Hotel, Piccadilly, London, W.1, at which Professor A. J. MURPHY, M.Sc., President, presided.

At the conclusion of the luncheon, the President presented the W. H. A. Robertson Medal to Mr. Christopher Smith and the Rosenhain Medal to Professor G. V. Raynor, D.Sc., D.Phil., M.A.

DISCUSSION OF PAPERS

The meeting was resumed, in the afternoon, at the Park Lane Hotel, Piccadilly, London, W.1, when the President, Professor A. J. MURPHY, M.Sc., occupied the Chair.

The following papers were presented and discussed. In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

"Influence of Oxide on the Pressing and Sintering of Copper Compacts", by T. P. Hoar, M.A., Ph.D., F.I.M., and J. M. Butler, B.A.

"Stress-Ageing Treatment and Its Effects on the Physical Properties of Copper-, Iron-, and Aluminium-Base Alloys", by R. F. Gill, B.S., E. A. Smith, and R. H. Harrington, Sc.D., P.E.

Wednesday, 14 March

At the resumed meeting, held at the Park Lane Hotel, Piccadilly, London, W.1, the President, Professor A. J. MURPHY, M.Sc., occupied the Chair.

SYMPOSIUM ON "METALLURGICAL ASPECTS OF THE COLD WORKING OF
NON-FERROUS METALS AND ALLOYS"

A general discussion, reported in this volume of the *Journal*, took place on the following papers. Professor F. C. Thompson, D.Met., M.Sc. (Vice-President) acted as rapporteur. At the conclusion of the session, a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

"Fundamental Aspects of the Cold Working of Metals", by Maurice Cook, D.Sc., Ph.D., F.I.M., and T. Ll. Richards, B.Sc., Ph.D., F.I.M.

"Lubricants for the Cold Working of Non-Ferrous Metals", by S. F. Chisholm, M.I.Mech.E., M.I.Mar.E.

"The Cold Rolling of Non-Ferrous Metals in Sheet and Strip Form", by C. E. Davies, M.I.Mech.E.

"Wire-Drawing Technique and Equipment", by F. T. Cleaver and H. J. Miller, M.Sc., F.I.M.

"The Deep Drawing and Pressing of Non-Ferrous Metals and Alloys", by J. Dudley Jevons, Ph.D., B.Sc., F.R.I.C., F.I.M.

Thursday, 15 March

The meeting was resumed at 4 Grosvenor Gardens, London, S.W.1, the President, Professor A. J. MURPHY, M.Sc., occupying the Chair.

DISCUSSION OF PAPERS

The following papers were presented and discussed. In each case a hearty vote of thanks to the authors was proposed by the President and carried with acclamation.

"Modification in Aluminium-Silicon Alloys", by B. M. Thall, M.A.Sc., Ph.D., and Professor Bruce Chalmers, D.Sc., Ph.D.

"The Solubility Relationships in the Aluminium-Sodium and Aluminium-Silicon-Sodium Systems", by C. E. Ransley, Ph.D., F.I.M., and H. Neufeld, B.Sc.

"Shearing of Metal Bars", by T. M. Chang, Ph.D., B.Sc., and Professor H. W. Swift, M.A., D.Sc.

"Shearing of Metal Blanks", by T. M. Chang, Ph.D., B.Sc.

The meeting then concluded.

COMMUNICATIONS METALLURGY.*

By EARLE E. SCHUMACHER,† B.S., MEMBER.

SYNOPSIS.

The lecture describes the function of the metallurgical department in a communications system. The need for metallurgical research and development, the origin of metals problems, the requirements imposed on metal components, and the integration of metallurgical developments into an operating communications system are given emphasis. It is shown how the solutions to problems may derive from previous experience, from empirical investigation, or from fundamental research.

Illustrative examples are given to demonstrate the complementary roles of engineering and research in correlating the properties of metals with their structure, and their structure with their history of fabrication.

It has been a high honour to receive, and a deep pleasure to accept, the invitation tendered earlier this year to address you at this time. I find it very gratifying that this, my first visit to your country, should be so occasioned.

Our respective countries share a common heritage of language and culture, and circumstances of recent memory have served to link us the more closely. We have been brought into frequent close collaboration on matters scientific and technical—a collaboration facilitated by the common language and marked by friendly co-operation.

This renders my present task at once pleasant and exacting: pleasant, because I know I speak to a group with allied problems and sympathetic viewpoint; and exacting, because of the responsibility I feel in representing before you the American worker in the metallurgical field. Nor have I felt easier in recalling the examples set on our side of the Atlantic before the American Institute of Mining and Metallurgical Engineers by Rosenhain, Desch, Evans, Edwards, Hutton, Hanson, Hume-Rothery, and most recently Orowan, to all of whom the American profession and industry are greatly indebted.

* Delivered at the Annual Autumn Meeting, Bournemouth, 18 September 1950.

† Chief Metallurgist, Bell Telephone Laboratories, Inc., Murray Hill, N.J., U.S.A.

I have tried earnestly to select for presentation before this group a subject of interest to you, allied to the principles of your Institute, and yet sufficiently novel and removed from the day-to-day round of professional activities to justify my presence here. Accordingly let us consider some matters that I believe I am in an advantageous position to bring before you and that were chosen in preference to some more academic subjects.

I should like you to see how some of the problems faced by a metallurgist in communications originate and how our group in particular approaches them. The research and development for our advances in communications are carried out in the Bell Telephone Laboratories, staffed by approximately 5000 technical and operating personnel. Of the technical staff, there are in my department the 30 metallurgists on whom, ultimately, rests the responsibility for the study of the metals and alloys comprising the telephone plant.

If any of you were to visit us I think you would observe three aspects of our work and organization that combine to characterize the department :

(1) The diversity of the Bell System plant is paralleled by the diversity of the problems we encounter and of the materials with which we are engaged.

(2) The results of our work are benefited by an "economic multiplying factor" in many instances of large magnitude. Lead cable sheathing—annual production 160 million pounds—is representative. A reduction of as little as a thousandth of an inch in sheath thickness by a new alloy or better processing can save a significant tonnage.

(3) If a common thread runs through our metal problems, it is to find a single material satisfactorily combining largely different, often at first glance incompatible, properties.

Our approach is dictated by the state of the art as we know it. We seek in principle to relate properties to constitution and structure, and then to control these through composition and fabrication. This, of course, cannot always be a deliberate and conscious process. Some problems are quickly solved by delving into accumulated experience. Others may require a development programme along empirical lines. Sometimes we find ourselves enmeshed in a full-scale research programme, extensive, intensive, and fundamental.

EXPERIENCE AND DATA : FIELD PROBLEMS.

Let us first examine the type of problem for which our stock of experience can supply a solution. Not surprisingly, we find that such problems generally originate under actual service conditions. Despite

the most thoroughgoing laboratory tests and field trials, it is obviously not always possible to anticipate fully the consequences of actual service on newly designed telephone equipment. New problems, requiring new designs or new materials, occasionally arise after equipment is installed.

Such an instance is the case of the coin boxes, which are an integral part of the public telephone illustrated in Fig. 1 (Plate I). The coin box lies behind the door seen at the bottom of the instrument, adjacent to the coin return slot. These numerous repositories of small change, though satisfactory for years, became increasingly inviting to the unscrupulous with increasing amounts deposited and wider distribution of the public telephones. Although the case-hardened steel doors of the collectors were difficult to open, a sufficient number were rifled and damaged to indicate a redesign. The favourite method at that time of removing the lock and getting at the money was to crack the case-hardened outer layer with a centre punch and then drill through the sheet-metal door into the lock mounting screws. A door was required economical to manufacture and of more discouraging resistance to drill and hammer.

A number of composite steels, as well as the very hard high-alloy steels, would have been physically satisfactory; their use was precluded by raw material and fabrication costs prohibitive for the quantities required. The final decision favoured a door of medium-carbon steel, drop-forged and subsequently hardened in final manufacture to a compromise temper making drilling difficult while retaining good impact strength. This door was designed to be used on existing housings to avoid replacing hundreds of thousands of coin collectors.

This satisfactory solution promptly instituted a new problem. When our nefarious but ingenious friends discovered that it was no longer feasible to drill the doors they changed their method of attack. Now they inserted a cleverly designed pry bar between the rigid door and housing and deformed the latter so that the door could be removed. The cash compartment portion of the housing was therefore redesigned as a forging which was comparable in rigidity to the door. This redesigned housing was used on all new installations as well as replacements of damaged collectors. This made it so difficult to pry open the box that thefts have become rare.

Changes in materials sometimes result from causes other than field service. They may, for example, be imposed by altered economic conditions. An enforced materials change on the simplest part can lead to surprising difficulties. For a period after the war steel was scarce while aluminium was plentiful. Hence it was suggested that the

material for the base of the "combined set"—a telephone unit incorporating essentially all the equipment required on the subscriber's premises—be changed from steel to an aluminium alloy. The base form is simply a flat sheet with turned-up edges and, since much of the finish could be omitted for aluminium, increased final cost was small. However, the original steel base, with the ringer mounted on it, performed an additional role; it acted as a partial shunt for the magnetic circuit. Without this shunt—and necessities of interchangeability dictated that the ringers be capable of mounting on either base—the ringers were intolerably loud. The outcome was the provision of a small auxiliary or sub-base of steel, illustrated in Fig. 2 (Plate I), for use with the aluminium base.

To the non-metallurgist it is not always evident that the processing of a material may be as important as its composition. Many years ago the gongs on the subscriber's set were on the outside of the box, and so were finished in matching black. The gongs were drawn from brass sheet and given a baked enamel finish. During a redesign, the gongs were moved inside the box and the finish omitted as a cost saving. After a short period it was found that the gongs not enamelled were inferior in tone quality, and furthermore, appeared, on testing, to be subject to season-cracking. Since both these troubles were indicative of residual stresses a stress-relief anneal was added to the process to replace the annealing incidental to the enamel-baking operation.

METALLURGICAL DEVELOPMENT: LEAD ALLOYS.

The instances cited illustrate, I believe, that the information needed to solve many problems has already been obtained in other investigations and accumulated in a category labelled "experience". Any of us here can well recall occasions when experience gained in one field finds frequent use in others. For example, we have long studied creep and fatigue characteristics of lead alloys, the principal incentive for so doing being furnished by the ever-present pressure to improve cable sheath and reduce its cost. Yet the applicability of this background is more general. A type of cartridge fuse installed in subscribers' cellars for lightning protection was found to be subject to frequent failure not due to melting from overload. Since variations in humidity could cause swelling and shrinking of the vulcanized fibre casing, fatigue was suspected. Fig. 4 (Plate II) shows a radiograph print of a random group of fuses removed from service after failure. The instances of simple melting are obvious. Those fuses showing a broad grey streak down the middle failed by extreme overload, as by lightning or power-line short circuit, resulting in an explosive vaporization. However,

there is an unduly high proportion of open circuits where no melting occurred, indicated by breaks in the solid wire. Microscopic examination of the original wires showed that one crystal often filled the entire cross-section, a circumstance conducive to fatigue failure. Experience with cable-sheath materials enabled us to select a grade of lead with an appropriate combination of minor elements, which on addition of a small percentage of antimony showed a reduced grain-size and improved fatigue resistance. This change reduced fatigue failures of these fuses to negligible proportions.

While this case was resolved by drawing on experience relative to a specific property of a specific alloy composition, it could hardly be expected that this circumstance would frequently recur. More often, the experience required is of a more general nature. We had learned, for example, from studies with dipping solders that arsenic, as shown in Fig. 5 (Plate III), has a marked grain-refining effect on lead-base alloys. This experience was translated into practice in improving wiping solders used at the splices between lengths of lead-sheathed paper-insulated telephone cables. Before describing the effects of arsenic, some comments on wiping joints and wiping solders may be helpful.

Some fourteen or more wiped soldered joints occur in every mile of lead-sheathed telephone cable. To join cables a lead sleeve of sufficient diameter to accommodate the bundle of spliced wires is slid into place at the junction, the ends of the sleeve are beaten in to conform to the circumference of the cable, and an air-tight and mechanically strong joint is formed at each end of the sleeve by manipulating a solidifying mass of solder into the desired shape. This last step is called the wiping operation.

The making of a successful wiped joint depends upon a satisfactory solder composition and considerable skill on the part of the splicer. The two factors are interrelated in that the more dextrous operators can produce satisfactory joints with compositions which could not be shaped by the average operator.

An investigation was made to modify the lead-tin type of wiping solder to meet practical requirements more fully than did earlier compositions. Through the addition of only 0.1% arsenic, two important beneficial effects are obtained. First, dross formation is reduced appreciably. Second, there is a grain-refining effect during solidification. With smaller amounts of dross formed, less time is required to skim the molten solder, and there is in the finished joints less included dross, a contributory source of porosity.

The grain-refining effect is illustrated in Fig. 6 (Plate III), which

compares the grain structures of a lead-tin solder and an arsenic-modified solder which have undergone similar handling and cooling treatments. The arsenic-bearing solder exhibits a finer and more uniform texture, associated with improved handling characteristics and freedom from porosity in the finished joint. Although the mechanism has not been definitely established, it is known that arsenic forms a new phase in the system, discernible in slowly-cooled solders at approximately 0.10% arsenic. It seems probable that this phase provides more numerous nuclei of crystallization around which the primary lead precipitates, or imposes barriers against the growth of the primary lead crystals, or both. With a greater number of primary crystals precipitated a greater surface is made available to which the molten eutectic may cling, producing a readily formable, more highly cohesive mass.

Even with the best of solders and techniques difficulty was encountered in obtaining hermetic seals at the massive wiped joints at large branched cable splices. Such joints as that of Fig. 22 are par-

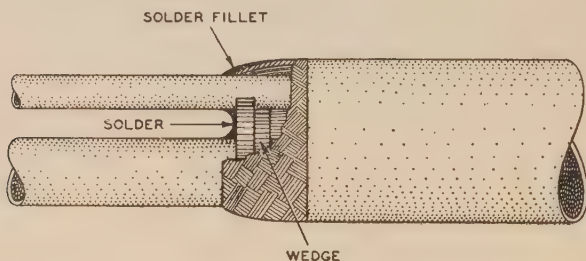


FIG. 22.—Assembly of Branched Cable Joints.

ticularly susceptible to porosity because of the large heat capacity of the heavy cables, sleeves, and locating plates or wedges required in the construction of this type. Solidification is therefore slow, which permits gravity movement of the liquid phase in the solder. Where there is appreciable liquid movement, there remain in the section from which the drainage began, lacy fissures that may connect and form through the joint a gas passage which is further enlarged by the localized solidification contraction of the remaining liquid. Fig. 7 (Plate IV) is a photomicrograph of an unetched section of a wiped joint showing a typical porous area.

Obviously, leaking fissures cannot be tolerated. Earlier practice consisted in rewiping the joint until gas-tight. Study of the problem indicated that a possible solution could be obtained by the application of a supplementary layer of a lower-melting solder to the surface of the

wiped joint using the heat residual in the joint to melt the extra solder. The way in which the sealing solder is applied is illustrated in Fig. 8 (Plate IV). The alloy is the ternary lead-tin-bismuth eutectic (lead 32, tin 15.5, bismuth 52.5%) and melts at 95° C. At temperatures between the 95° C. eutectic and the 184° C. solidus of the wiping solder, the sealing eutectic readily wets the latter and appears to be drawn into the capillary-like fissures in the joint, thus effecting a seal.

Having insured sound joints, a further precaution is taken to prevent subsequent entrance of moisture into our inter-city cables. Dry gas under moderate positive pressure is maintained inside the cables. If a leak occurs, the escaping gas prevents water from entering, and the drop in pressure operates an alarm gauge. However, the continuous pressure introduces substantial circumferential stresses in the sleeve, particularly in those of larger diameter. Since the sleeve must not burst nor even distend to any appreciable extent in the course of a normal lifetime of many years, the sleeving must primarily be creep-resistant.

The sleeving alloy and its safe working stress for prolonged loading were selected after extensive tests conducted in the creep laboratory. There is provision for investigating more than 500 specimens at one time, and some special tests have been under way for over 10 years, although a satisfactory evaluation of creep properties can be made in about one year. Creep studies showed a suitable sleeving material for the 200–300 lb./in.² stress range involved to be a commercial grade of lead containing small percentages of copper, nickel, and silver. The last element in particular both age-hardens the material and increases the recrystallization temperature. It is interesting that this low-alloyed lead is much superior in creep to the lead 1%–antimony so extensively used for the cable sheath, while much inferior in fatigue. It is the superiority of the lead–antimony alloy in fatigue that dictates its choice in sheathing applications.

Lead–calcium alloys, of course, have also shown dramatic creep resistance. Our interest was first aroused by their attractive possibilities for cable sheath, but their electrolytic properties have proved equally intriguing. Work in this latter field has resulted in the application of lead–calcium alloys to the manufacture of grids for storage batteries for float usage—that is, under stand-by conditions with maintenance of a constant charge. The presence in the grid structure of elements electropositive to lead, such as the almost universally used antimony, promotes sulphation and self-discharge. It was to be expected that calcium would eliminate this hazard, as it is electronegative

to lead, and the existent extensive studies of lead-calcium alloys showed that it could impart the desired mechanical rigidity to the grid. Increase in the calcium content over that used in the experimental cable-sheath alloys produced more than adequate strength, and batteries with grids so made have not merely shown the expected lower self-discharge rate, but, more important, have demonstrated a longer life than the antimony batteries. Our lead-calcium test batteries still retained the original 120% of the rated capacity after 13 years on test, while comparable lead-antimony batteries dropped to 75% capacity after 9 years and to less than 25% after 13 years.

A development, forming a corollary to the experimental work on lead-calcium cable sheath and battery-grid alloys, was directed to a rapid analytical method for the control of calcium content in production, although it is not usual for a metallurgical department to engage in the development of analytical methods.

The experimental lead-calcium cable sheath was specified to contain $0.028 \pm 0.005\%$ of calcium for the proper age-hardening characteristics; lead-calcium battery grids are specified to contain $0.075 \pm 0.010\%$ of calcium. The composition in the melting kettle must be continuously controlled within these limits in the course of casting and replenishing with lead and addition alloy.

We had observed in the laboratory that the film forming on the surface of solidifying lead-calcium varies with calcium content in a very sensitive manner as illustrated in Fig. 9 (Plate V). By casting test samples in air having controlled carbon dioxide and water content, it is possible to analyse within the cable-sheath composition range to a precision of $\pm 0.002\%$. To extend the range to the battery-grid compositions, a weighed sample is titrated with a standard lead-antimony alloy. The antimony precipitates the calcium as an intermetallic compound and the end-point is determined from a surface appearance consistently characteristic of 0.005% calcium and independent of atmosphere. Fig. 10 (Plate V) shows surfaces resulting from deviations of only 0.001% calcium either side of this end-point. The method is as precise as a wet analysis and requires only a small fraction of the time.

This study was a departure from our usual pursuits, but was a valuable by-product prompted by the previous studies and resulting in an analytical method economical for production. It is, further, unusual in involving a liquid-metal titration and is unlikely to have originated in other than a metallurgical laboratory.

We shall now consider some problems relating to the cable sheath itself and illustrating further the necessity of empirical investigation

in a development programme. For many years cable sheath has been identified with one or another lead alloy. The recent war has broadened our thinking in this respect as in so many others. The critically short supply of lead in the years immediately following the war placed a premium on the rapid development of alternative cable-sheathing materials. Based on two decades of earlier experimentation with laminated structures, Alpeth, an aluminium/polyethylene composite was developed. This consists of a corrugated aluminium sheath wrapped about the cable core, over which assembly is extruded the polyethylene outer covering, as shown in Fig. 11 (Plate VI). The aluminium acts not only as an electrical shield but also as an auxiliary moisture barrier.

The cyclic stresses resulting from temperature fluctuations have prompted our fatigue studies on all types of cables and cable-sheathing materials, and our testing equipment has been designed to impose strains of the magnitudes encountered in the field, at cyclic rates sufficiently accelerated to compress twenty to thirty years of service into one or two months of test. The machine used for assembled lead-sheathed cable is shown in Fig. 12 (Plate VI). The Alpeth sheath had to be tested similarly, but its enhanced flexibility over lead-sheathed cables rendered existing machines unsuitable. Fig. 13 (Plate VII) shows an instrument designed and built for testing this particular structure. Three lengths of cable are made to conform to predetermined opposite and equal circular arcs by the motion of contoured wooden blocks. The cyclic motion from left to right in the horizontal plane is imparted by the crank, driven through reducing gears by the motor.

With the aid of this instrument we have found that fatigue failure in Alpeth sheath occurs in the aluminium inner layer, but only after an elapsed life of five to ten times that of lead alloy sheath. The polyethylene jacket is amazing in not yet having failed in any of the fatigue tests conducted. No fatigue problems are foreseen with this structure, since the cracks in the aluminium moisture barrier are of minor importance so long as the polyethylene cover remains intact.

This fatigue test illustrates one conducted on a structure itself under simulated service conditions. Many of our tests are conducted on component parts, but in these cases the results are for the material rather than for the particular apparatus part, and can be useful in contributing to the general field of fatigue of metals and its underlying mechanism.

We cannot, of course, afford to confine our fatigue programme within the shelter of laboratory conditions. We conduct extensive

outdoor tests at our field laboratory (Chester, N.J.). The existence of this laboratory results from the insufficiency of extrapolating to service conditions the data acquired from a laboratory experiment of limited scope and indicates the distance we have yet to travel in developing laws of creep and fatigue enabling accurate prediction of service performance.

I have so far discussed in a general way some problems either originating in the field, or anticipating service conditions. These problems draw upon our general metallurgical experience and also add to it, both in the accumulation of necessary data, and in directing our attention towards needed research.

METALLURGICAL DEVELOPMENT : FABRICATION.

One field where an empirical rather than a research attack is necessarily used is metals fabrication. Our knowledge of the governing laws of the structure and properties of cast metals and worked metals is still too elementary; we cannot yet infallibly predict a fabrication schedule. Empirical development is requisite. Our metals-processing laboratory is engaged in such specialized projects as casting odd structures in refractory metals, rolling hard foils, heat-treating in magnetic fields, and drawing wire of hair dimensions. Development in

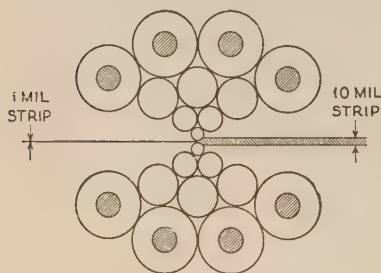


FIG. 23.—Schematic Representation of Roll Arrangement in the Rohn Mill.

fabrication practice must often proceed in parallel with development of new circuit elements and telephonic components. Sometimes the sole metallurgical problem in connection with a new apparatus development is one of fabrication. We find this particularly true with magnetic alloys. In addition to their sensitivity to processing practice these materials are frequently required by our communications engineers in physical forms that tax facilities and ingenuities to the limit.

There is a demand, for example, for very thin foils of less than a thousandth of an inch in thickness, and often of exceedingly hard materials. These can be handled on the Rohn mill which we obtained from Germany in 1936 and later modified to increase its range of reduction. Fig. 23 illustrates some of the features of this type of mill. The heavier rolls back up the innermost working rolls, which are 0.160–0.300 in. in dia. and slightly crowned. Tension is applied to the material

both on entering and leaving the rolls. Reductions as high as 90% per pass, and final thicknesses down to 0.0002 in., can be achieved. This is attributed primarily to the high pressures resulting from the very small contact area of the small work rolls in this mill design. The mill in operation is shown in Fig. 14 (Plate VII). Since the change in length during a pass may be as much as tenfold, the strip surfaces are accelerated on passage through the rolls. This acceleration, and the high rolling pressures, apparently near the yield point of the rolls themselves, engender a sliding friction limiting the permissible reduction per pass.

To make foil 0.0001 in. and less in thickness in a minimum of passes, a new and rapid method was devised. Thin strip is processed to approximately 0.002 in. by conventional methods, then passed through a plating bath to double the original thickness by electrodeposition of copper on each surface. The plated strip is heated to approximately 400° C. and plunged into a bath of light oil. The porous copper coating soaks up and stores oil in its many capillaries. This procedure is analogous to the method employed for oil-impregnating the sintered, powder metal bearings. Continuous porous bearing surfaces are produced over the entire length of a strip which may run into thousands of feet. Rolling can then proceed with reductions up to 90%, as for example from 0.002 to 0.0002 in. This is accomplished in a single pass through the rolls of the cluster mill. Without the oil-impregnated porous copper coating the same total reduction would require four to twelve passes, depending on the material being rolled. After rolling, the plated coating is dissolved by an acid bath. The final Permalloy foil is only 0.0001 in. thick.

Now it sometimes happens that fabricating difficulties can be overcome by a slight composition change, provided this does not endanger fulfilling the final physical requirements. For example, the 50% cobalt-50% iron alloy has magnetic properties that make it of value for telephone-receiver diaphragms and armatures. At room temperature in this composition range, as shown in Fig. 24, the magnetic induction is greater than the value for either of the components. Also of interest, but less desirable here, is the fact that the electrical resistivity of the 50 : 50 alloy is lower than would be expected from the usual behaviour of alloys. The binary alloy can be worked hot, but is extremely brittle when cold. This precludes the production of thin sheet by cold rolling. The limitation can be overcome, however, by adding a few per cent. of a third element such as vanadium. The modified alloy can be worked hot, and after a quench from a high temperature can also be cold rolled to thin sheet. The electrical resistivity is advantageously increased and the magnetic characteristics are not significantly impaired by the

vanadium addition required for cold working. Vanadium retards the ordering occurring in these alloys at approximately 700°C ., and therein lies an explanation for its action. The disordered plastic arrangement of atoms in the ternary alloy is retained by quenching and facilitates cold rolling.

The alloy of 49% each of cobalt and iron and 2% vanadium in the form of a disc 0.010 in. thick, is the diaphragm of a telephone receiver of which there are now millions. This composition has been specified for use in the form of a ring, also 0.010 in. thick, as the armature of a new type of receiver.

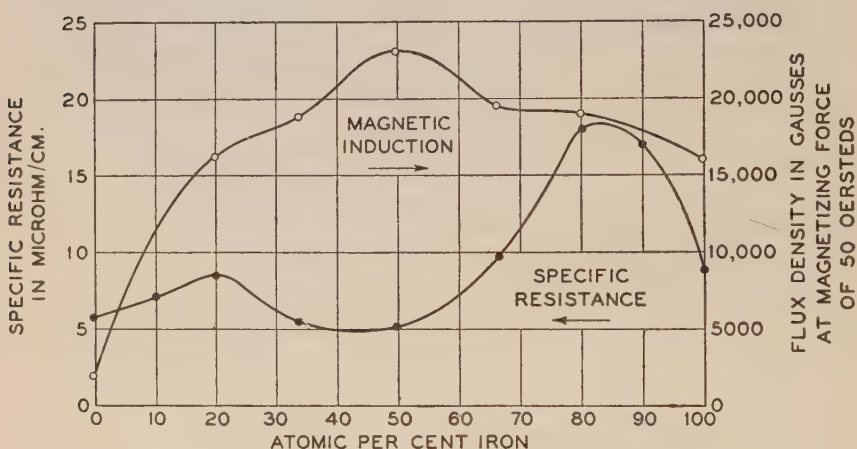


FIG. 24.—Variations of Properties with Composition in Iron-Cobalt System.

You may be interested in the various components of the new receiver illustrated in Fig. 15 (Plate VIII). In the centre are the vanadium Permendur armature and the impregnated cloth dome which serves as a diaphragm. The component immediately to the left is a cup-shaped Remalloy magnet. Its development is an interesting story and I should like to outline its history for you in some detail. Initially we were given the following requirements: first, minimum magnetic characteristics for the material of 9000 gauss residual induction and 300 oersteds coercive force; second, sufficient strength to withstand a severe drop test without cracking; third, an unusual shape with thickness tolerances of $-0, +0.005$ in.; and finally, a strict cost limitation.

In considering these stipulations and the available permanent-magnet alloys, it appeared that a casting of one of the Alnico compositions would satisfy the magnetic requirements but perhaps not the

drop test. Nor did it seem feasible to grind the castings to the close tolerance within the cost limit. These suspicions were confirmed on preparing and testing trial lots of magnets, both sand cast and precision-cast by the lost-wax process. Experimentation with powder metallurgy as a last resort demonstrated that uniformity of wall thickness in such a thin section could not be economically achieved.

Since it seemed unlikely that the processing methods which proved far too costly for preparing Alnico magnets could be applied more advantageously to other permanent-magnet alloys, it was decided to investigate hot forging as a method of fabrication. This, of course, was not applicable to Alnico, but did show promise in forming cups from blanks of Remalloy, despite the handicap of a narrow hot-forging temperature range. Remalloy, a carbon-free permanent-magnet alloy of the dispersion-hardening type, has the nominal composition molybdenum 17, cobalt 12, and iron 71%; and has nominal magnetic characteristics of 11,000 gauss residual induction, and 230 oersteds coercive force. The latter is well below the 300 minimum required for this design. In preliminary experiments it was determined that by increasing the molybdenum content of Remalloy to 20%, using pure raw materials and special processing, a coercive force averaging 350 oersteds could be obtained without any sacrifice of hot forgeability. The latter was of particular importance in view of the need for hot rolling ingots to 0.100 in. strip and the subsequent drastic hot forging to a cup shape. However, the laboratory conditions under which these experimental tests were conducted held carbon to less than 0.02%, which is impractical for commercial production using standard-grade raw materials. Further studies showed that by the addition of titanium to fix carbon and by the use of aluminium as a deoxidizer in place of the customary silicon-bearing deoxidizer, it was possible to meet both the 300-oersted minimum coercive force and the required residual induction using commercial-grade raw materials. Thus it became practicable to produce commercially in 6-ton lots an alloy especially tailored to meet the design requirements and the cost objective.

METALLURGICAL RESEARCH : CONTINUING PROJECTS AND PROBLEMS.

Great impetus lies behind the types of investigation just described. Increasing the life of cables, minimizing maintenance costs, controlling magnet quality, reducing fabricating costs on items made in the millions, all contribute substantial and immediate economic gain resulting in improved service to the subscriber at lower real cost over the years.

Such advances serve to offset the present greatly increased labour costs and thus aid to stabilize rates.

We cannot, however, be content to await problems as they arise, or satisfy ourselves merely to keep pace with the demands of present developments. There are fields of investigation which by their magnitude alone demand years of continuing study which is carried well into the province of pure fundamental research; there are problems both present and anticipated for which we can give no pat answer, but must undertake long-range programmes of development and study; there are the promising concepts, the new ideas, offering rewards for patient research which we cannot afford to ignore. This condition of healthy dissatisfaction with the *status quo* will continue in our case so long as human demand requires communication service more extensive, more efficient, or more economical than the present affords.

Thus within an electrical communications laboratory, we are required to conduct many programmes of metallurgical research, both experimental and theoretical, which, irrespective of the origin of the problem, are fundamental in nature. Such programmes may not always answer the questions that gave rise to them, either at once or in the foreseeable future; but we have found them fruitful and valuable in the light they may cast on many obscure problems, in the new ideas they produce, and in the contributions they make to the science of physical metallurgy.

Research advances in a well-established and relatively settled field are often made when a new point of view or a new technique is brought to bear on a problem. I would like to illustrate this point by describing briefly the results of a recent investigation in which metallurgical background and techniques were applied to the problem of electrical contact erosion.

The importance of electrical contacts in telephone communications hardly needs mention. Hundreds of millions of electrical contacts must operate reliably for calls to go through. One of the most persistent obstacles to successful operation of contacts is electrical erosion which may take many forms.

One form, called bridge erosion, was singled out for study. As contacts open a direct-current circuit, the last-to-separate regions of the contacts melt, forming a tiny bridge of liquid metal. When the bridge breaks—actually it more nearly explodes—a transfer of metal to the negative contact takes place. Repetition of this action results in a mound on one contact and a crater in its mate.

The eroded areas of contacts damaged under controlled conditions by bridge erosion were examined on the metallurgical microscope at high magnification. Fig. 16 (Plate IX) shows microscopic craters

typical of such an area in a palladium-40% silver contact operated at 5 amp. The mean crater dia. is 13 μ .

Measurements of the dimensions of the microcraters in many such contacts led to a general relationship involving crater size, contact material, and current. Further analysis suggested that materials which differed greatly in crater size could be paired in contacts in such a way as to eliminate bridge erosion. Subsequent testing confirmed the analysis. Fig. 17 (Plate IX) provides an illustration of the effect. The upper contact pair illustrates bridge erosion typical of like pairs of precious metals, resulting from 1,000,000 operations at 5 amp. The lower pair shows no crater or build-up, only negligible pitting of the surfaces, after 2,000,000 operations at 5 amp. Transfer has been prevented in the second case by using platinum-20% iridium for the negative contact, gold for the positive. Similar results can be obtained with many other combinations of contact materials.

Oddly enough, this method for preventing material transfer by bridge erosion, while effective over a considerable range of currents, was found to be inapplicable to the weak currents of telephone circuits. Thus, in this particular case, our research results may bear more fruit outside the telephone field than within it.

Contacts are connective elements in the electrical communications system. The entire system is a gigantic network of various circuit elements, of which one of the most fundamental is the familiar resonant circuit. The purely electrical resonant circuit, finding multitudinous use in filters, equalizers, and all kinds of electronic apparatus, is built up of capacitors and inductances and has but passing interest for us on this occasion. I may mention but briefly that inductance cores of metallic oxides, prepared by ceramic techniques, are being improved to the point where built-up filters employing them can offer serious competition as circuit components to the more expensive quartz plate filters. Some experimental forms of these cores are shown in Fig. 3 (Plate I). They combine high permeability with high electrical resistivity. The result is inductances of low core loss and high efficiency, which are used in sharply-tuned resonant circuits capable of operation over an extended frequency range.

Of more interest to us here to-day is the mechanically resonant circuit. It is analogous to the purely electrical resonant circuit, and in fact can be and is treated mathematically in terms of its electrical equivalent. A mechanical device operated only by vibrational signals of a narrow frequency range is obviously of great utility for remote switching and relay operation, particularly when the actuating signal can be sent over the air, or superimposed on a transmission line carrying

a variety of other electrical information, whence it can readily be filtered out when desired.

A device of this sort, called a vibrating-reed selector, is used, for example, in signalling in the mobile radio telephone by which the operator of an automobile can call or be called by any other telephone in the nation. The vibrating-reed selector consists of two reeds brazed to a base to form a little tuning fork as shown in Fig. 18 (Plate X). The ends of the tines are surrounded by a magnetic coil. When the current in the coil is of the same frequency as the natural vibration frequency of the tuning fork the reeds vibrate and make a contact. Such tuned vibrating devices must maintain a vibrational frequency

independent of temperature. It is then necessary that the stressed portion have a modulus of elasticity substantially independent of temperature. It must have as well an appreciable magnetic permeability, also independent of temperature.

The magnetic properties of commercially available isoelastic materials vary more than we like. For this reason we have initiated an investigation of the moduli and thermoelastic coefficients of ferromagnetic materials. The moduli and temperature co-

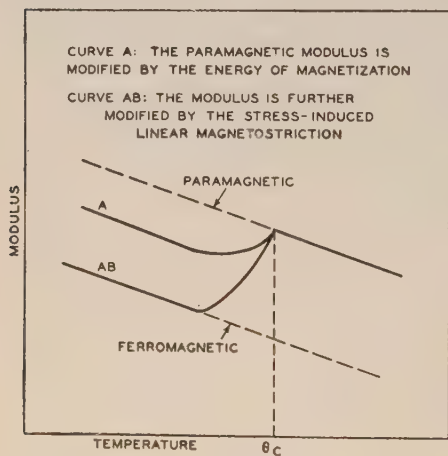


FIG. 25.—Effect of Ferromagnetism on Modulus/Temperature Relationship of Iron-Nickel Alloys Containing 36–52% Nickel.

efficients of binary iron-nickel alloys, we found, are very sensitive to fabrication and heat-treatment. For example, a 57% iron–43% nickel alloy, when fully annealed, has a highly negative thermoelastic coefficient. This alloy can be made nearly isoelastic over the desired temperature range (-40° to $+80^{\circ}$ C.) by a procedure of cold work followed by a stress-relief anneal at 400° – 600° C. This difference is explained in Fig. 25. The top line represents the decrease of the elastic modulus with increasing temperature usual for a paramagnetic material. Suppose that these iron-nickel alloys are above the Curie temperature. On cooling, the modulus/temperature curve begins to deviate from the usual paramagnetic behaviour with the onset of ferromagnetism at the Curie



FIG. 1.—Public Telephone.

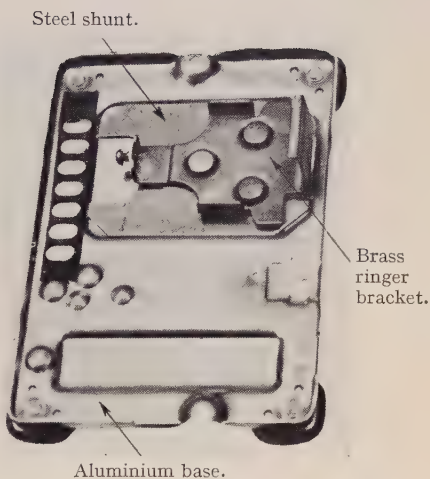


FIG. 2.—Combined-Set Base Plate Equipped with Magnetic Shunt for Ringer.



FIG. 3.—Experimental Inductance Cores of Metallic Oxides.

[To face p. 16.]

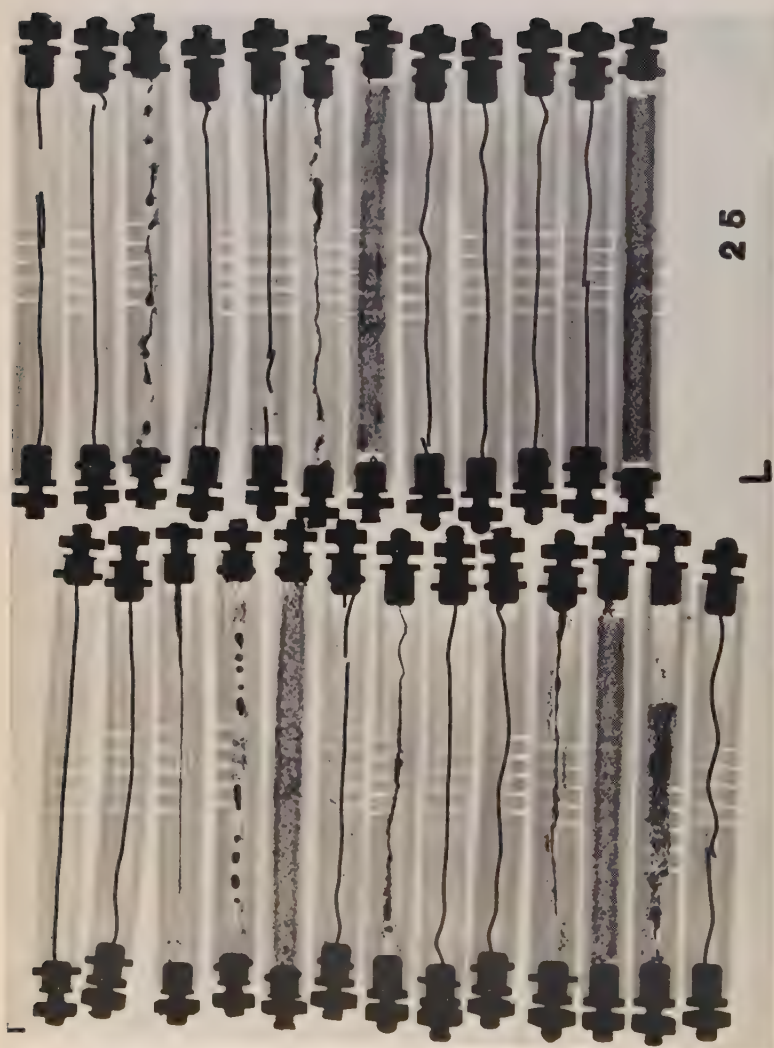
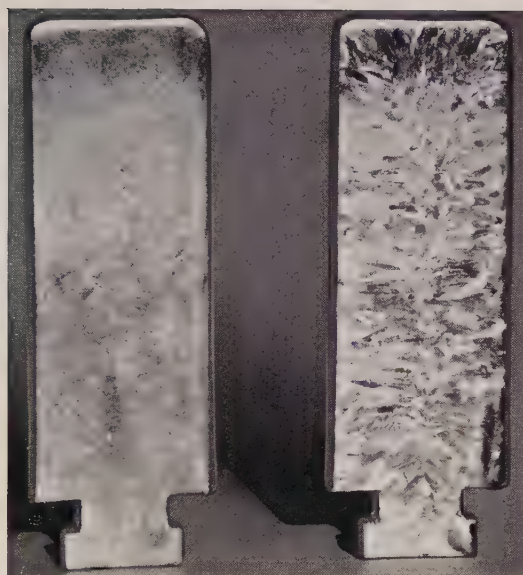


FIG. 4. — Radiographic Print of Types of Failure in a Random Group of Replaced Fuses.



0.01% Arsenic.

Arsenic-free.

FIG. 5.—Effect of Arsenic on Grain-Size of Lead-Base Coatings on Iron Parts.



0.10% Arsenic. $\times 4$.



Arsenic-free. $\times 4$.

FIG. 6.—Effect of Arsenic on Dendrite-Size in 38% Tin-62% Lead Wiping Solder.

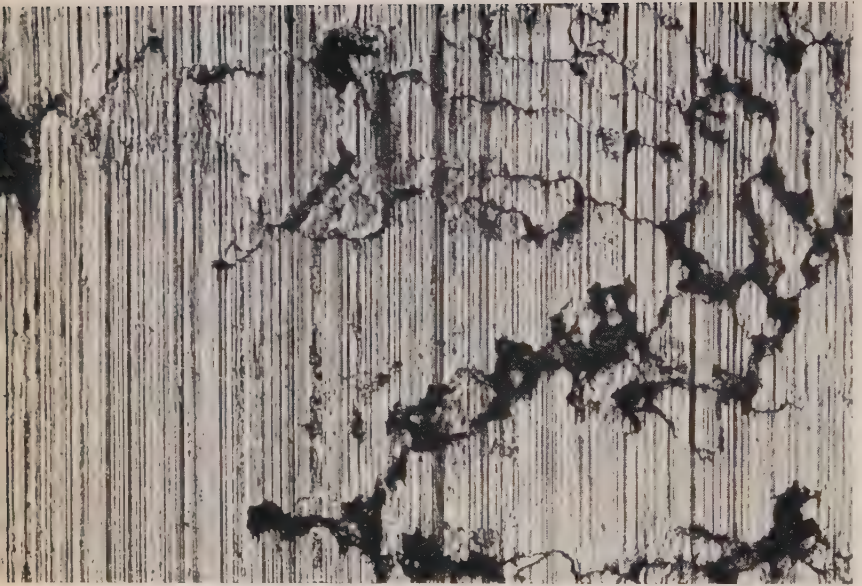


FIG. 7.—Fissures in Wiped Solder Joint. Unetched. $\times 600$. Reduced one half in reproduction.

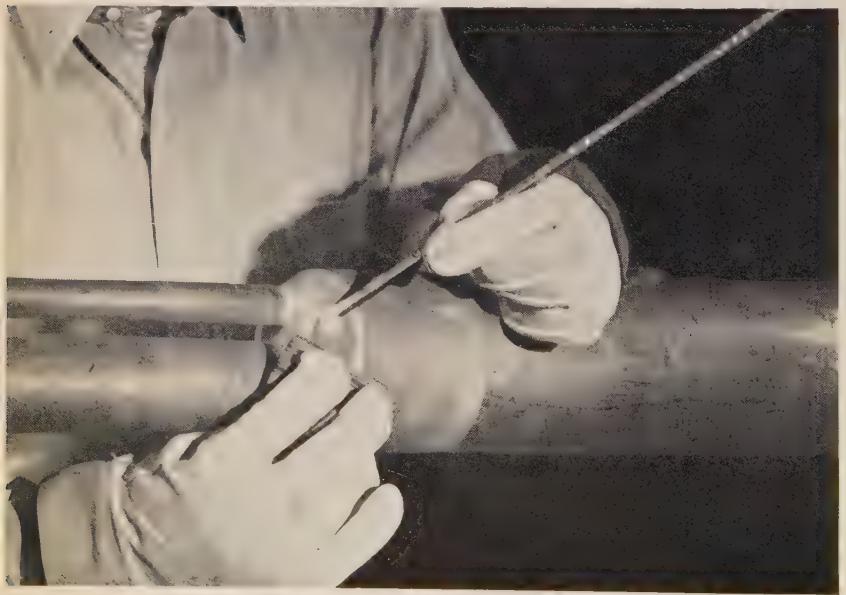


FIG. 8.—Applying Sealing Solder to a Branched Cable Joint.

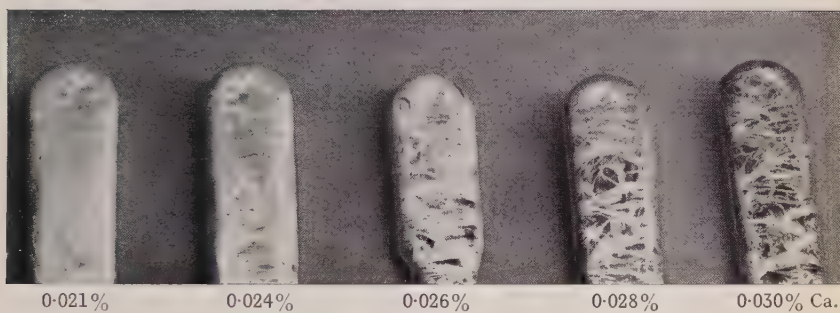


FIG. 9.—Surface Appearance of Lead Castings as a Function of Calcium Content. $\times 1$.
Reduced by one-quarter in reproduction.



FIG. 10.—Surface Appearance of Lead Castings as Calcium Content is Varied through End Point. $\times 2$. Reduced by one-quarter in reproduction.



FIG. 11.—Aluminium/Polyethylene Sheath Structure in Alpeith Cable.

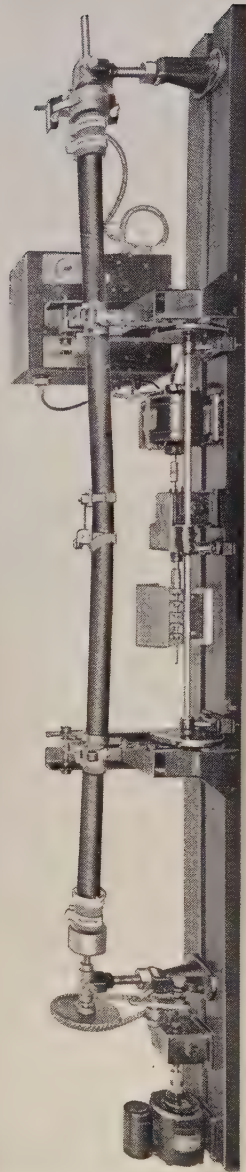


FIG. 12.—Machine for Fatigue Testing 6-ft. Sections of Lead-Sheathed Cable.

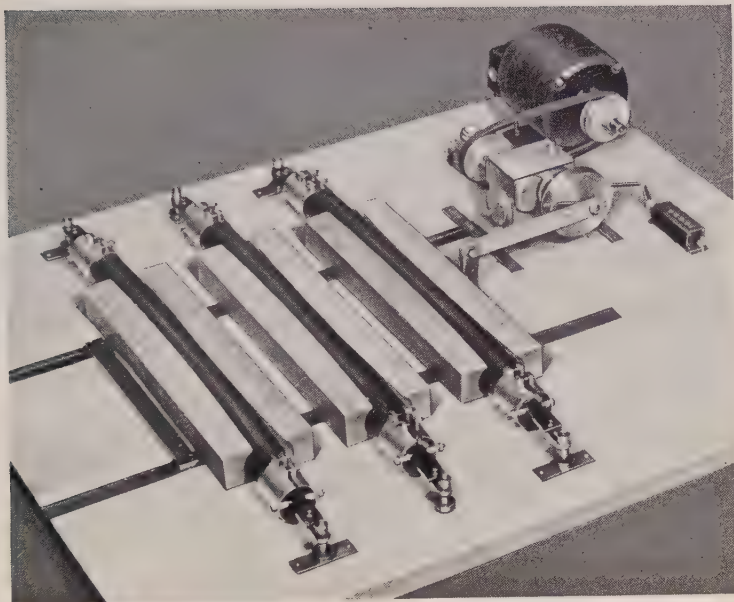


FIG. 13.—Machine for Fatigue Testing Alpeth Cable.

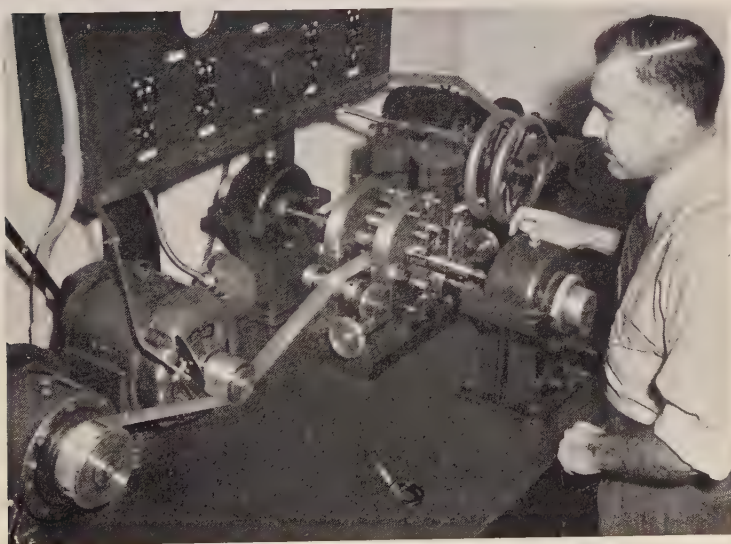


FIG. 14.—Rohn Mill in Operation.

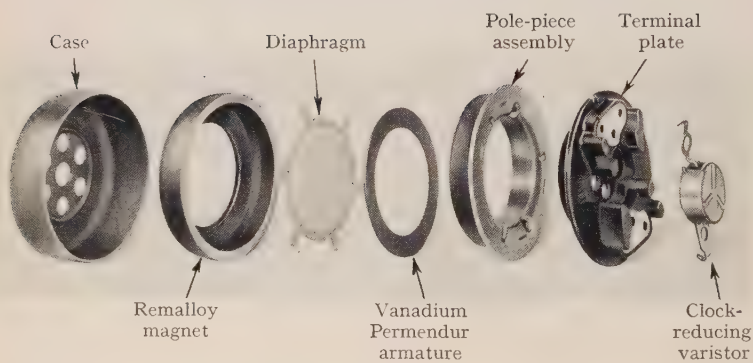
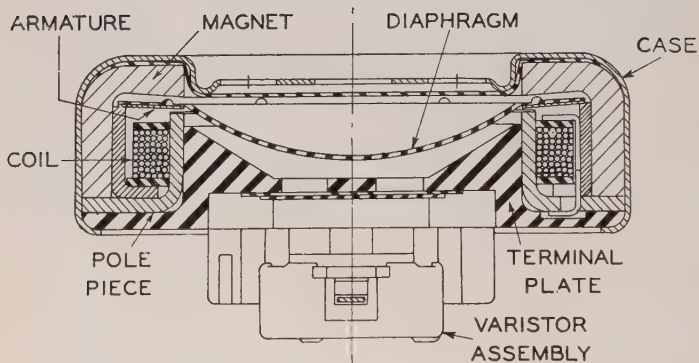


FIG. 15.—Receiver Unit.

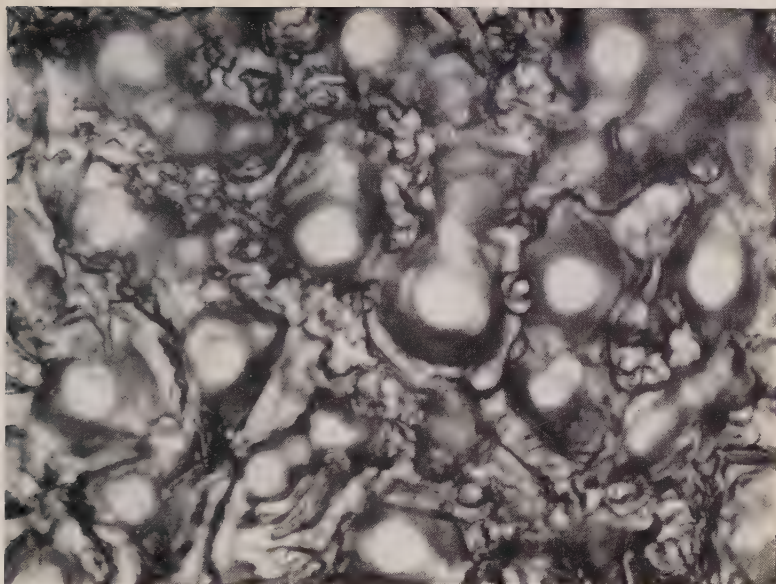


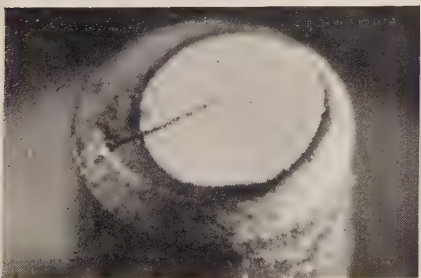
FIG. 16.—Microscopic Craters Produced by Bridge Erosion of a Palladium-Silver Contact. Mean dia. of craters $13\ \mu$.



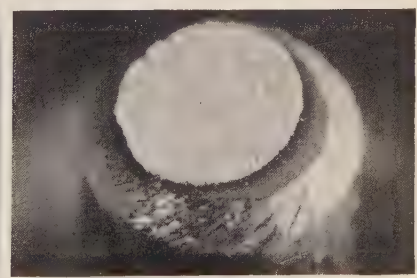
+



-



+



-

FIG. 17.—Contact Pairs after Operation under Bridge Erosion Conditions.

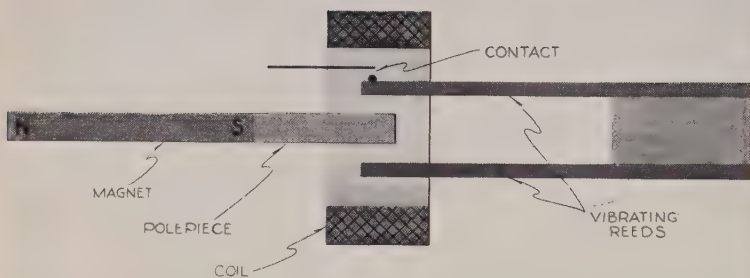


FIG. 18.—Schematic Representation of Vibrating-Reed Selector.

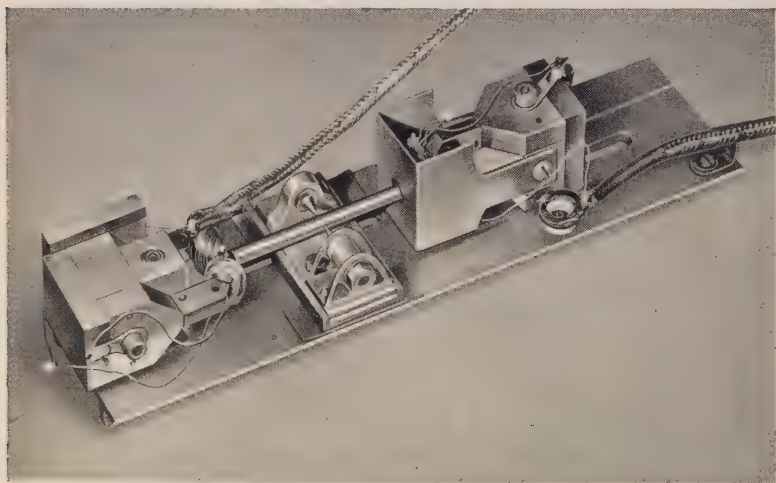
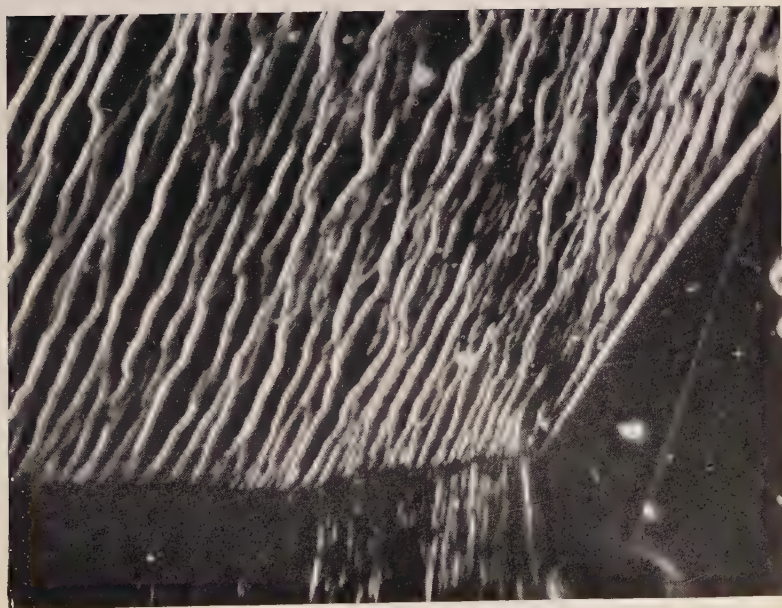
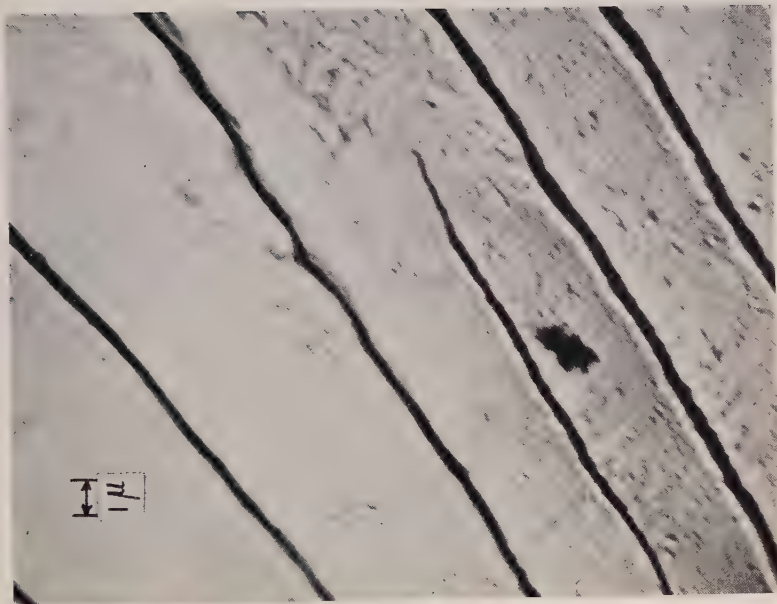


FIG. 19.—Apparatus for Dynamic Measurement of Young's Modulus.

E = modulus (dynes/cm.²) = $4\rho l^2 f_r^2$; ρ = density (g./cm.³); l = length (cm.);
 f_r = resonant frequency (c./s.).



(a) Dark-field illumination. $\times 800$.



(b) Electron micrograph. $\times 6000$.

FIG. 20.—Slip Markings in Chromium.
Reduced by one-fifth in reproduction.

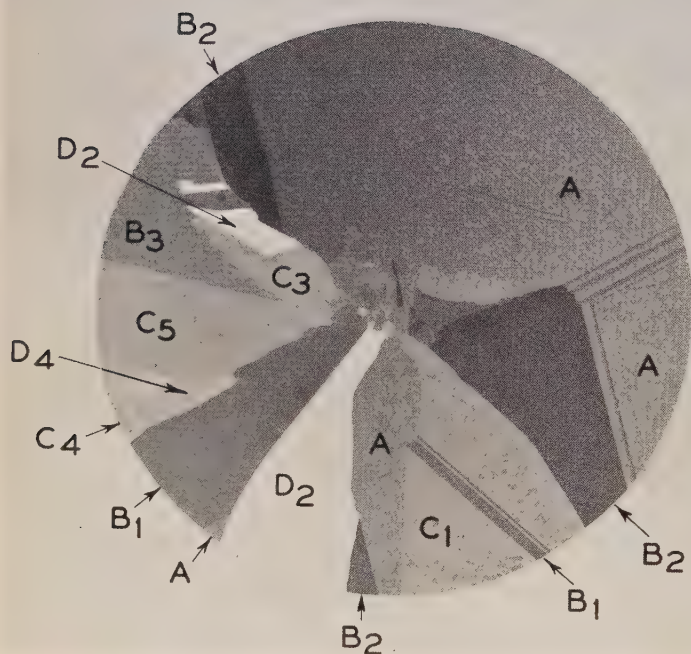
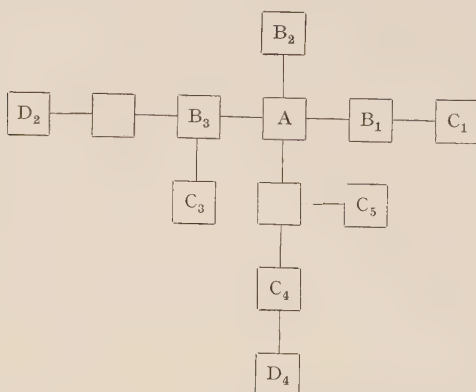


FIG. 21.—Etched Transverse Section of Germanium Ingot. $\times 5$. Reduced by one-third in reproduction.



Schematic Representation of Twin Relationships in Section shown above.

temperature. The deviation is the result of two effects. First the energy of magnetization lowers the modulus, and if this were the only effect, curve *A* would be observed. But the stress-induced linear magnetostriction further lowers the modulus, so that actually curve *AB* is observed. Cold working largely eliminates the magnetostrictive contribution, and the modulus/temperature relationship more nearly resembles curve *A*. Comparing curve *A* with curve *AB*, the former has a more extensive range of isoelasticity. The low-temperature anneal is only to stabilize the modulus. Investigation along these lines is continuing to develop materials with better mechanical properties, still smaller thermoelastic coefficients, and to adjust the magnetic properties to desired values.

Out of this research, as so often occurs, another study of equal interest has arisen. The investigation of Young's modulus over a temperature range for the tuned-reed project required the construction of a special apparatus, shown in Fig. 19 (Plate X). With this device we determine the resonant frequency in longitudinal vibration of a rod of the material held at a temperature controlled within 1° C. The specimen, supported at the nodal point, is driven magnetically over a range of frequencies by the coils shown; the resonant frequency is determined from the output amplitude of the magnetic current induced in the pick-up coils enclosed in the shield. Young's modulus is then calculable by a well-known expression from the frequency at resonance. With well-designed equipment, changes in the elastic modulus as small as 0.01% can be detected. This has proved to be a very good method for studying transformations in metals. With it we have investigated the transition occurring in chromium near room temperature, and the rather remarkable results are shown in Fig. 26. This transition is seen to occur over a wide temperature range with the maximum rate at 37° C. The modulus change is known to correlate with changes in electrical resistivity, thermal expansion, and damping capacity.

Another really challenging field of research is the study of the properties of refractory, or high-melting-point, metals. In our constant inquiry into new materials of potential value, our attention was attracted by the work done at the United States Bureau of Mines and other places on the preparation and properties of pure titanium. The very high strength-to-weight ratio of this metal, combined with a high melting point and excellent corrosion-resistance, makes it of great interest. From our experience with titanium we predict that with increasing availability it will become an important metal in communications. We have rolled this material to foil 0.00012 in. thick.

Chromium, mentioned previously, is another refractory metal of

great potential value. Any extension of its use must await its being rendered amenable to ready fabrication. The plastic deformation of chromium for the purpose of producing wire and sheet has been studied

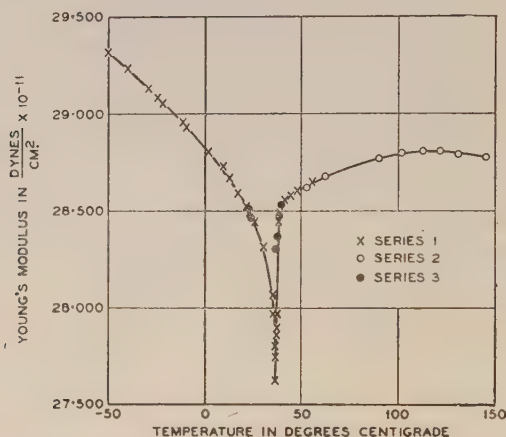


FIG. 26.—Effect of Temperature on Young's Modulus of Chromium.

by a number of investigators. It has been observed by Kroll and confirmed in our laboratory that purified chromium can be rolled at temperatures in the region of 1300° C. The metal is brittle at room

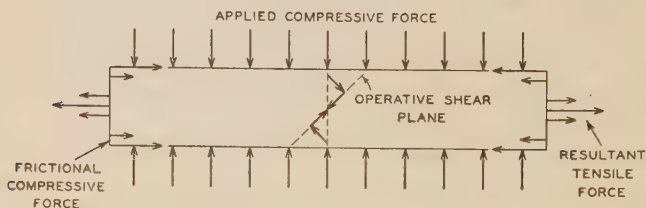


FIG. 27.—Schematic Representation of Stress System in Specimen of Chromium during Plastic Deformation.

temperature. To our knowledge no plastic flow in chromium at room temperature has been reported except that associated with hardness tests. We have found, however, that a certain amount of plastic flow can be induced in purified chromium by compressing it between hardened steel blocks, as indicated in Fig. 27. This system of deforma-

tion results in compressive stresses both normal to the contact surfaces and, as the result of friction, parallel to them in the vicinity of contact. The effect is to decrease the tensile stress normal to the shearing planes in the region of flow. By using this system of stressing, we have compressed an annealed specimen of purified chromium from a thickness of 0.139 in. to 0.123 in. (11.5% reduction). It was observed that a previously polished face, which had been parallel to the axis of compression, contained slip markings as shown at 800 magnifications by dark-field illumination in Fig. 20 (a) (Plate XI). Greater detail is revealed by the electron micrograph at 6000 magnifications shown in Fig. 20 (b). These features are slip markings, since they were eliminated by subsequent polishing and etching.

The wavy directions of these markings in the plastically deformed chromium indicate that at room temperature more than one slip plane may be operative, as in the case of body-centred cubic iron. These planes have not yet been identified in the case of chromium. This work suggests that chromium can be deformed plastically at room temperature by compression combined with hydrostatic pressure.

A further field of research in which we have a basic interest includes the semi-metals, silicon and germanium. Until recently these elements have not been studied extensively by metallurgists. The use of these materials in communications in such devices as the point-contact rectifier and the transistor has, of course, resulted from, as well as prompted, extensive study of their properties. Their reduction and preparation are essentially metallurgical procedures involving familiar considerations of atmosphere control; of thermal gradient, ingot structure, and impurity segregation; and of constitution and heat-treatment.

All important to these semi-conductors is their content of trace elements. Metallurgists have established a basic relationship between the position of an element in the periodic system and its effect on the electrical conductivity of silicon or germanium. Elements of Group III introduce negative carriers, those of Group V, positive carriers. When both are present their effects cancel, each element nullifying the conductivity of the other. The concentrations involved are extremely low. One atom of antimony added to 100,000,000 of germanium can double the conductivity.

As metallurgists you can appreciate some of the problems involved in preparing uniform ingots from these impurity-sensitive materials. An example is given by the solidification of an alloy of germanium containing 0.00078% antimony. As Fig. 28 shows, segregation has caused most of the added antimony to appear in the upper extremity of

the ingot, which is the last part to freeze. The concentration in the body is as low as about 1% of the average. Since the ingot was solidified slowly from the bottom upwards, segregation was controlled, making it possible to cut reasonably uniform sections from the ingot. In the case of silicon, we have obtained electrically uniform ingots by equalizing the rates of segregation of the elements boron and phosphorus. This was achieved by adjusting the total concentrations of boron and phosphorus to an experimentally predetermined ratio.

Our present research programme on silicon and germanium covers a considerable area: the effects of heat-treatment, the nature of the

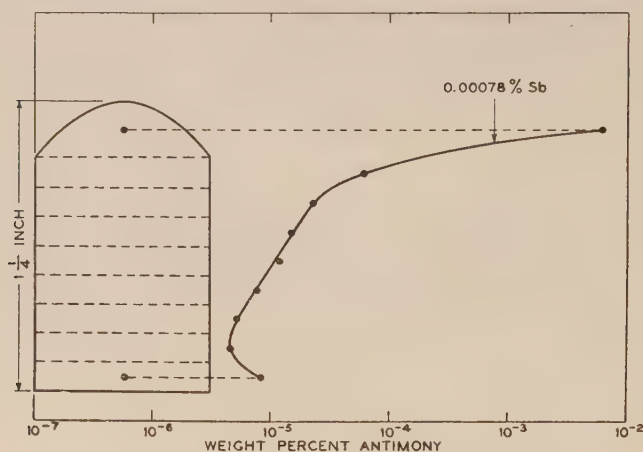


FIG. 28.—Distribution of Antimony in Ingot of Germanium Containing 0.00078% Antimony.

freezing process and of the crystal structure, the solubility and diffusion of other elements—in short, the typical problems encountered by the physical metallurgist on many fronts.

We have of late been interested in orientation relationships in germanium ingots, and the study has led to rather amazing results. Examination of a transverse slice cut from an ingot of germanium solidified progressively from the bottom discloses extensive twin relationships. A slice, taken about midway in a cylindrical ingot approximately $\frac{3}{4}$ in. in dia. and $1\frac{1}{2}$ in. in length, and etched to delineate different orientations, is shown in Fig. 21 (Plate XII). The orientations of the regions designated with letters were determined by a Laue X-ray back-reflection method and represented on stereograms. The orientation relationships of the components indicated were determined

by comparing the values for the nine angles between the three respective cube poles of each orientation with the values calculated in a formal treatment of octahedral multiple twinning in cubic crystals. Germanium, which is diamond cubic in structure, has the octahedral twinning habit. The set of values for the nine angles is distinctive of the order of twinning. Confirmation for a multiple twin relationship is obtained from the determined indices of the mirror planes, which exist for all orders of twinning through the third and for some of the fourth.

The interesting twin relationships shown schematically in the lower part of Fig. 21 were found for the section shown above the schematic diagram. Most of this slice was made up of orientation A appearing in widely separated regions. Of the four possible first-order twins of A , three were present in this slice and are designated by B with subscripts. Four second-order twins of A are designated by C with subscripts. It is worth emphasizing that two of these, C_4 and C_5 , are second-order of A through the first order missing in this section. Two regions, designated D with subscripts, are third-order twins of A . D_2 is a sixth-order twin of D_4 . All orientations found were ascribable to multiple twinning, as if the orientations in this section originated earlier in solidification from a single nucleus.

The presence of extensive multiple twinning together with the absence of other orientations appears to be a characteristic result, in many instances, of solidification of germanium. Fertile conditions for twinning probably exist in the array of atoms in the diamond cubic structure. The extent of twinning is probably associated with constraint imposed by an irregular growth front in solidification. This may also be in part due to the attempt of the solidifying region to attain the orientation most favourable to the growth direction. The nucleus for a twinned orientation could arise through a stacking fault on the octahedral plane.

A rectifier material, older and more familiar in the sense of extensive industrial application, is copper oxide in conjunction with its parent metal. Typifying a kind of tangent study that results when research is diverted for a time from the main problem by an interesting lead in another direction, is the story of the thallium-copper rectifier.

In the communications field, we have for some time utilized as circuit elements a great number of copper oxide varistors of the type discovered by Grondahl. A peculiarity of this type of rectifier is the dependence of quality on a particular type of commercially produced copper, namely that obtained from ore deposits in Chile by leaching and electrowinning, using insoluble anodes.

Over the years, as many of you know, trouble has been encountered in the commercial production of copper oxide rectifiers, and much study has been devoted to tracking down the elusive factor or factors responsible for the unique quality of this copper and for the variability of rectifiers made from different batches showing little or no compositional differences.

In some of our early studies, we had conducted an extensive spectrographic investigation of copper samples on which we had accumulated varistor-experience data. From this work, there was found only a single compositional variation which could be correlated in any systematic way in our investigation, and even here the possibly significant differences were so minute as almost to escape detection. The element which appeared to be significant was lead. An investigation made of its effect in Chilean copper when added in controlled amounts showed that it produced a very high junction resistance with only slightly increased forward resistance—a favourable alteration. Later it was discovered that the effect of lead was erratic and caused a high degree of ageing in varistors. By this time another study had been launched of its companion element, thallium, and in this instance the desired improvement was obtained without the deleterious effects noted for lead.

Since the thallium-copper varistor was first produced, it has gone through all the stages from research on the mechanism of its action, development of methods for its preparation, pilot-plant manufacture of major experimental quantities, to final commercial manufacture on a large scale. To-day, in addition to the normal copper oxide varistor, our manufacturing division, the Western Electric Company, produces thallium-copper varistors in quantity for a number of special uses, such as, for example, the telephone click-reducer, where its unique voltage/current relation ideally suits the purpose. Fig. 15 (Plate VIII) shows this small unit that is incorporated in the new combined telephone set to eliminate the hazard of acoustic shock.

Thus, we trace this development from a deviation from our general studies of the basic principles of the copper oxide varistor through all the steps to large-scale manufacturing, and we find that, although we have a new and most useful product, we have not solved the original problem we had set up for ourselves—that of determining why Chilean copper differs from other types of copper when made into rectifiers, and why variability in rectifier quality appears from time to time in Chilean copper itself.

Yet I would not have you believe that the basic research programme was interrupted, or that the fundamental studies were unfruitful. On

the contrary, these studies were continued vigorously and have aided materially in our conception of rectifier action. It is true, however, that before these more basic studies had yielded information that would enable us to duplicate the characteristics of the thallium-copper varistor, this circuit element had been a part of telephone equipment for a number of years.

CONCLUSION.

It is an advantage to the metallurgist in communications that his view is of necessity broad and diverse. His scope embraces field engineering problems as well as fundamental research projects and includes the range of physical metallurgy from engineering properties to solid-state physics. Communications metallurgy is given interest by this diversity of subject matter; scientific significance by the depths to which this matter must be probed; and economic importance by the quantities of metals with which it is concerned.

What I have intended to illustrate in describing these studies is the origin of the problems confronting the metallurgist in communications; the organization of the effort towards their solution; and the places that experience, empiricism, and research occupy in that organization.

In some few cases there may be evident the scientific aspects of our profession in consciously relating composition and fabrication with constitution, structure, and properties. All too often links in the logical chain are missing. I submit that a fruitful philosophy of metallurgical endeavour will purpose to forge these links: to use experience when available, empiricism when necessary, and both as clues to the research which alone can transmute art into science.

ACKNOWLEDGEMENT.

It is evident that even the studies I have cited are not the work of one man; they exemplify the efforts of our group over a period of years. I should like now to acknowledge the contributions of these men and to thank them for their co-operation in the preparation of this lecture.

THE SOLUBILITY RELATIONSHIPS IN THE 1268 ALUMINIUM-SODIUM AND ALUMINIUM- SILICON-SODIUM SYSTEMS.*

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JUNIOR MEMBER.

SYNOPSIS.

The solid solubility of sodium in aluminium has been determined by direct measurement of the amount dissolved when high-purity aluminium is immersed in liquid sodium. The solubility is approximately 0.002% in the range 650°–550° C. and appears to have a very small temperature coefficient. The data obtained allow a calculation to be made of the rate of diffusion of sodium in solid aluminium. The liquid-miscibility boundary in the binary system has also been redetermined; the monotectic composition is found to be 0.14% sodium, and the solubility of sodium in liquid aluminium increases smoothly from this value to 0.25% at 775° C.

It is shown that when aluminium containing silicon in solid solution is heated in liquid sodium, a ternary compound is formed as a surface layer or sub-scale. By means of experiments in which aluminium strips with different silicon contents were exposed to the action of sodium for prolonged periods, it has been possible to derive approximate values for the concentration of silicon and sodium in solid solution in equilibrium with this compound at various temperatures. The equilibrium silicon contents determined are: 600° C., 0.15%; 550° C., 0.04%; 500° C., 0.01%; the corresponding sodium contents are in the range 0.0016%–0.0005%. Since the compound is stable to high temperatures (above 800° C.), a similar procedure could be used to determine the liquidus isothermals in the primary field of the compound. Only one compound has been observed; its composition has not been precisely determined, but appears to be based on $[\text{NaAlSi}_{1.25}]$ or $[\text{NaAlSi}_{1.33}]$. On the basis of the liquid-solubility results obtained, a tentative diagram for the aluminium-silicon-sodium system is put forward, indicating a ternary eutectic at about 0.017% sodium.

I.—INTRODUCTION.

UNTIL quite recently the published data relating to the aluminium-sodium system were very meagre. Scheuer¹ was the first to detect and measure any solubility of sodium in liquid aluminium; prior to his work the elements were reported to be completely immiscible both above and below the melting point of aluminium. The experimental method he employed was to heat aluminium with an excess of sodium under hydrogen until equilibrium was attained, then to quench the

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melt and determine the sodium content of the aluminium-rich layer. The analysis was carried out by the well-known procedure, also developed by Scheuer, which involves heating the metal in air to about 900° C. and then leaching out the alkali from the surface of the cooled sample. Scheuer estimated the solubility of sodium to be 0.10% at 700° C., 0.115% at 750° C., and 0.128% at 800° C. He also made similar measurements of the solubility in one or two alloys over the same temperature range. It is now known, however, that this method for the determination of sodium is liable to give low results, and the solubility values he obtained are probably erroneous because of this limitation.

The work described in the present paper was initiated about two years ago, but the investigation has been protracted because of the tedious nature of some of the measurements. In the meantime, a paper by Fink, Willey, and Stumpf² has appeared. These authors determined the boundary of the liquid-miscibility gap by a method similar to that of Scheuer, except that their melts were made under a positive pressure of argon instead of hydrogen. They also determined the monotectic temperature and the hypo-monotectic liquidus by both direct and differential thermal analysis. The equilibrium diagram they put forward shows a monotectic temperature of 659° C. and a monotectic composition of 0.18% sodium. The solubility of sodium in liquid aluminium was found to decrease slightly with increasing temperature. Fink and his co-workers attempted to determine the solid solubility by resistivity measurements, but were unsuccessful because it was found that the resistance variations were less than the probable experimental error; from micrographic examination, however, it was concluded that the solubility was less than 0.003% sodium, even at temperatures approaching the monotectic.

The main interest of the present authors in the aluminium-sodium system was to gain some information on the solid-solubility limits, and for this purpose an entirely different experimental method was adopted from that used by Fink, Willey, and Stumpf. The results obtained allow a rough calculation to be made of the rate of diffusion of sodium in the metal. The liquid-miscibility boundary has also been redetermined, and the data show a more orthodox increase of solubility with increasing temperature, instead of the retrograde solubility found by Fink and his co-workers.

The experiments on the solid solubility of sodium in aluminium indicated that when silicon was also present a relatively insoluble compound, probably ternary, was formed under certain conditions. The effect of silicon was therefore explored in some detail, and the results

of this work led to an examination of the liquid-solubility relationships in the ternary system. A tentative equilibrium diagram, based on these solubility measurements, is put forward for the ternary system; this has an important bearing on the general problem of the modification of aluminium-silicon alloys, but this aspect is not discussed in any detail.

II.—SOLUBILITY OF SODIUM IN SOLID ALUMINIUM.

After rejecting various orthodox methods for the determination of solid solubility on the score of lack of sensitivity, it was finally decided to adopt the simple technique of measuring the amount of sodium absorbed by the solid metal in equilibrium with molten sodium. Although this procedure was direct and had obvious advantages, it was necessary to exercise great care in the preparation of samples for chemical analysis, since it would have been possible for surface contamination to lead to gross errors.

1. *Materials.*

Although in the later stages of the work a number of "doped" batches of super-purity metal were used, most of the early results were based on one batch of super-purity metal (J.R.1) which was also used for some hydrogen-absorption experiments to be described in another paper.³ The following analysis of this metal was made:

Si, %	Fe, %	Na, %
0.0025	0.0005	0.0002

The sodium used for the solution experiments was of normal commercial purity. It was stored dry and was freshly trimmed before use.

2. *Experimental Procedure.*

The sample or samples of metal to be saturated were inserted into a stout mild-steel bomb, a sufficient quantity of freshly trimmed sodium to cover the sample was pressed in, and the stopper of the bomb immediately inserted and screwed down very tightly. The bomb was approximately 1 in. in dia. and 4 in. high internally.

Since very long saturation times were necessary (up to 650 hr.), two and sometimes three bombs were usually placed together in a furnace, which was maintained at the required temperature ($\pm 3^\circ \text{C.}$) by means of a Foster controller. Three types of aluminium specimen were used:

(1) Large cylinder, 15 mm. in dia., 60 mm. long. Only one of these could be charged into a bomb for each test.

(2) Small cylinder, 8 mm. in dia., 60 mm. long. Three of these specimens were usually inserted into each bomb.

(3) Sheet, 1.5 mm. thick. The charge in this case usually consisted of six strips each 20×60 mm., bound together in a pack, with suitable spacing pieces so that the molten sodium had free access to all surfaces.

After heating for the desired period, the bombs were removed from the furnace and allowed to cool freely in air. The specimens were removed by washing out with alcohol, and appeared to be only moderately etched in the process. The weight of sample taken for sodium analysis was about 8–10 g., and consisted of half of one of the large cylinders, a complete small cylinder, or two sheet specimens. The analysis was carried out by high-vacuum distillation; in this method the sodium is separated from the bulk of the sample by evaporation at about 900° C., and then determined by means of zinc-uranyl acetate, using a volumetric finish. This procedure is described in detail in a separate paper.⁴ In normal replicate tests on homogeneous samples (e.g. cast blocks or similar massive metal) the standard deviation in the sodium analysis is $\pm 0.00022\%$ when the sodium content is in the range 0.01–0.001%. In general the results obtained in the present experiments conformed to this error, but there were instances in which the scatter was considerably higher. In order to obtain consistent and reproducible results, it was found necessary to etch the samples fairly deeply in dilute hydrochloric acid and to take great care that there was no contamination of the surface.

3. *Theoretical Considerations.*

Before accepting any solubility limits established by the suggested method (i.e. saturation of the metal by inward diffusion of a solute) it is necessary to be satisfied on the following points:

(1) That the time allowed for diffusion is adequate for the attainment of equilibrium; in the experiments described, a 95% saturation of the sample could be taken as a reasonable end-point in the diffusion process.

(2) That there is no internal precipitation of compounds formed between the solute entering the metal and any other elements already present as impurities.

The second point will be considered more fully in Section IV. As far as full saturation of the specimens is concerned, the mathematical treatment of the diffusion of sodium into the cylindrical and sheet specimens is quite straightforward. Because of the various probable errors in the measurements it is adequate to use approximate solutions of the Fick equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

The appropriate solution in the case of the cylindrical specimens (treated as infinite in length) is :

$$\bar{C} - C_0 = [C_s - C_0] \left[1 - \frac{4}{5 \cdot 8} e^{-\frac{5 \cdot 8 D t}{a^2}} - \frac{4}{30 \cdot 5} e^{-\frac{30 \cdot 5 D t}{a^2}} - \dots \right] \quad (2)$$

where \bar{C} (wt.-%) is the mean concentration of sodium in the cylinder at time t (sec.), C_s (wt.-%) is the saturated solubility of sodium in the metal, i.e. the constant concentration at the surface for $t > 0$, C_0

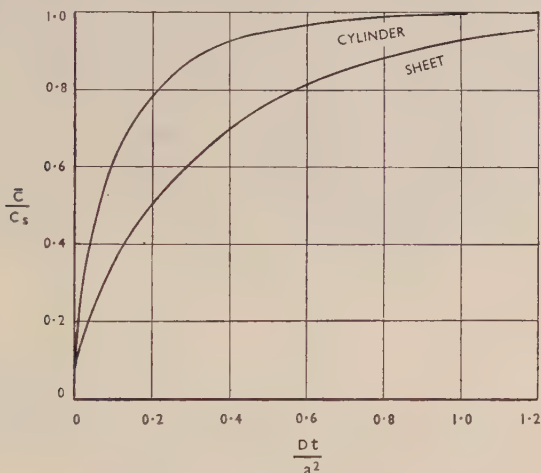


FIG. 1.—Diffusion into Cylindrical and Sheet Specimens.

KEY.

- \bar{C} = Mean concentration for time t (sec.).
- C_s = Saturated solubility.
- D = Diffusion coefficient.
- $2a$ = Diameter of cylinder or thickness of sheet.

(wt.-%) is the initial concentration of sodium in the metal, a (cm.) is the radius of the cylinder, and D (cm.²/sec.) is the diffusion coefficient.

The 1.5 mm. sheet can be treated as an infinite plate, and the solution in this case is :

$$\bar{C} - C_0 = [C_s - C_0] \left[1 - \frac{8}{\pi^2} \sum_{m=0}^{m=\infty} \frac{1}{(2m+1)^2} e^{-\frac{D(2m+1)^2 \pi^2 t}{4a^2}} \right] \quad (3)$$

where $2a$ is the thickness of the sheet and the other symbols are as in equation (2).

These two equations can be solved rapidly, and with sufficient accuracy for the present purpose, by a graphical method. This is

demonstrated in Fig. 1, in which the value of the saturation fraction $\frac{\bar{C}}{C_s}$ (or $\frac{\bar{C} - C_0}{C_s - C_0}$, if the initial concentration of sodium in the metal is significant) has been plotted as a function of the dimensionless parameter $\frac{Dt}{a^2}$ for the two cases of the infinitely long cylinder and the infinite plate. By the use of these curves the value of D can be derived immediately if the percentage saturation, the time of diffusion, and the radius or thickness of the specimen are known.

It was important to establish at an early stage in the work whether the solubility of sodium in aluminium is structure-sensitive or not, i.e. is a function of grain-size. Such dependence has been noted in at least one other system (bismuth in copper⁵) which has some features in common with the aluminium-sodium system. In fact, the theory advanced by Voce and Hallows,⁵ which ascribes the embrittlement of copper by bismuth to the formation of a monatomic film of the element at the grain boundaries, may feasibly be put forward to account for the supposed deleterious effect of sodium on the hot-tensile properties of aluminium alloys. In the present experiments, however, the grain-size in the super-purity specimens after exposure to sodium was generally very large ($\gg 1$ mm.), and it could then be estimated that the amount of sodium required to produce a complete intercrystalline monatomic film in such metal was of the order of only 0.00002%. This was negligible in comparison with the sodium contents which were actually observed.

4. Results.

It soon became evident that the solid solubility of sodium in aluminium is in the region of only 0.002%, and the tests were therefore limited to temperatures approaching the monotectic (659° C.), since it was expected that the solubility would be at a maximum at this temperature. The results obtained are summarized in Table I. The analyses quoted are based on duplicate or triplicate determinations.

It will be seen that the figures for final sodium content show a fairly regular variation with respect to time and temperature. Since the times required for 95% saturation of the 15 mm. cylinder, 8 mm. cylinder, and 1.5 mm. sheet were in the ratio of 42 : 12 : 1, it was easy to judge from a comparison of the results on the different-sized specimens whether the uptake of sodium by the metal had attained approximate equilibrium. As Table I shows, the final absorption at all the temperatures investigated was 0.0020% sodium with a scatter of about $\pm 0.0004\%$. The one exception was in the tests at 635° C., but only

TABLE I.—Solid Solubility of Sodium in Aluminium.

Temperature, ° C.	Type of Specimen	Time, hr.	Final Sodium Content \bar{C} , wt.-%	Diffusion Coefficient D , cm. ² /sec. $\times 10^9$
650	15 mm. cylinder	70	0.0009	90
	15 "	140	0.0010	60
	8 "	312	0.0021	...
645	8 mm. cylinder	288	0.0016	30
	8 "	264	0.0019	80
	1.5 mm. sheet	264	0.0020	...
635	15 mm. cylinder	168	0.0012	70
	15 "	284	0.0014	60
625	8 mm. cylinder	336	0.0012	10
	8 "	504	0.0018	30
	1.5 mm. sheet	652	0.0018	...
600	8 mm. cylinder	204	0.0010	11
	8 "	336	0.0024	...
	1.5 mm. sheet	336	0.0016	...
550	1.5 mm. sheet	334	0.0009	0.6
	1.5 "	457	0.0014	1.2
	1.5 "	625	0.0018	2.0

15 mm. cylinders were used in these and insufficient time was allowed for anything like full saturation to be attained. It was therefore concluded that this value (0.0020% sodium) may be taken as a reasonably accurate figure for the solid solubility over the whole of the temperature range investigated; it follows, therefore, that the temperature coefficient must be relatively small.

Taking this value as the equilibrium solubility, C_s , over the range 650°–550° C., it is possible to calculate the corresponding diffusion coefficient, D , from the data for partially-saturated specimens. In doing this, it is necessary to discard values which from inspection represent near-saturation conditions, since quite small analytical errors will in these circumstances produce very large errors in D . The diffusion coefficients which have been derived are given in the right-hand column of Table I, and are plotted logarithmically against the reciprocal of the temperature in °K. in Fig. 2. These measurements are, of course, subject to considerable error and the results are somewhat scattered. However, a straight line has been drawn through the points to accord with the standard diffusion relationship:

$$D = D_0 e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where E (cal./g.-atom) is the activation energy of the diffusion process,

D_0 is a constant with the dimensions $\text{cm.}^2/\text{sec.}$, and T is the temperature in $^{\circ}\text{K}$. From the slope of the line, the value of E is found to be 32,000 cal./g.-atom. The value of E calculated from a single value of D ($1 \times 10^{-8} \text{ cm.}^2/\text{sec.}$ at 600°C.) by means of the semi-empirical Langmuir-Dushman equation is found to be 29,500 cal./g.-atom, which is in quite good agreement with the experimental result.

Also plotted in Fig. 2 are the mean values for the diffusion of silicon in aluminium, taken from the published data.⁶ It will be seen that although the rates of diffusion of sodium and silicon are of the same order, the diffusion of sodium is rather more rapid at temperatures

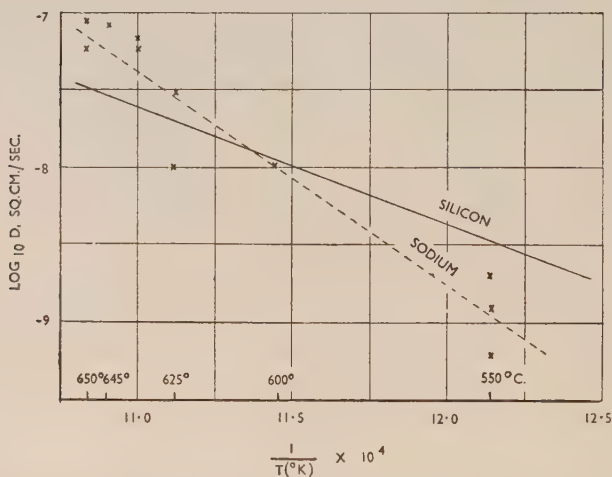


FIG. 2.—Diffusion of Sodium and Silicon in Aluminium.

above 600°C. , and slower at temperatures less than 600°C. This comparison is of interest when considering the uptake of sodium by aluminium containing silicon in solid solution, and will be referred to again in Section IV.

III.—SOLUBILITY OF SODIUM IN LIQUID ALUMINIUM.

The method used to determine the liquid-miscibility boundary was similar to that used by Scheuer,¹ and by Fink, Willey, and Stumpf,² i.e. fusion of aluminium in the presence of excess sodium, rapid quenching of the melt, and analysis of the aluminium-rich layer.

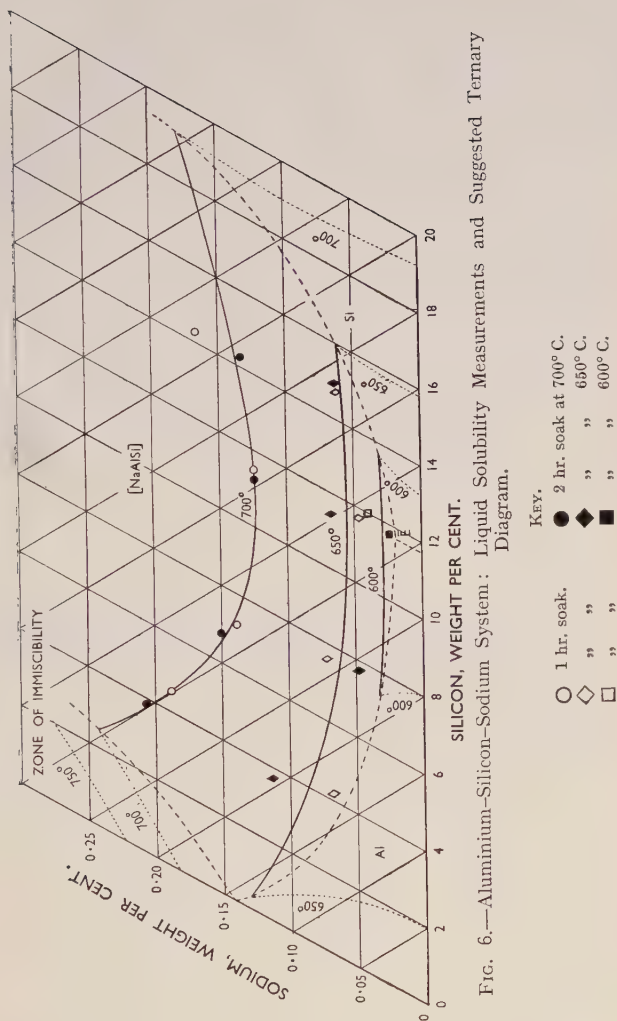


FIG. 6.—Aluminum-Silicon-Sodium System: Liquid Solubility Measurements and Suggested Ternary Diagram.

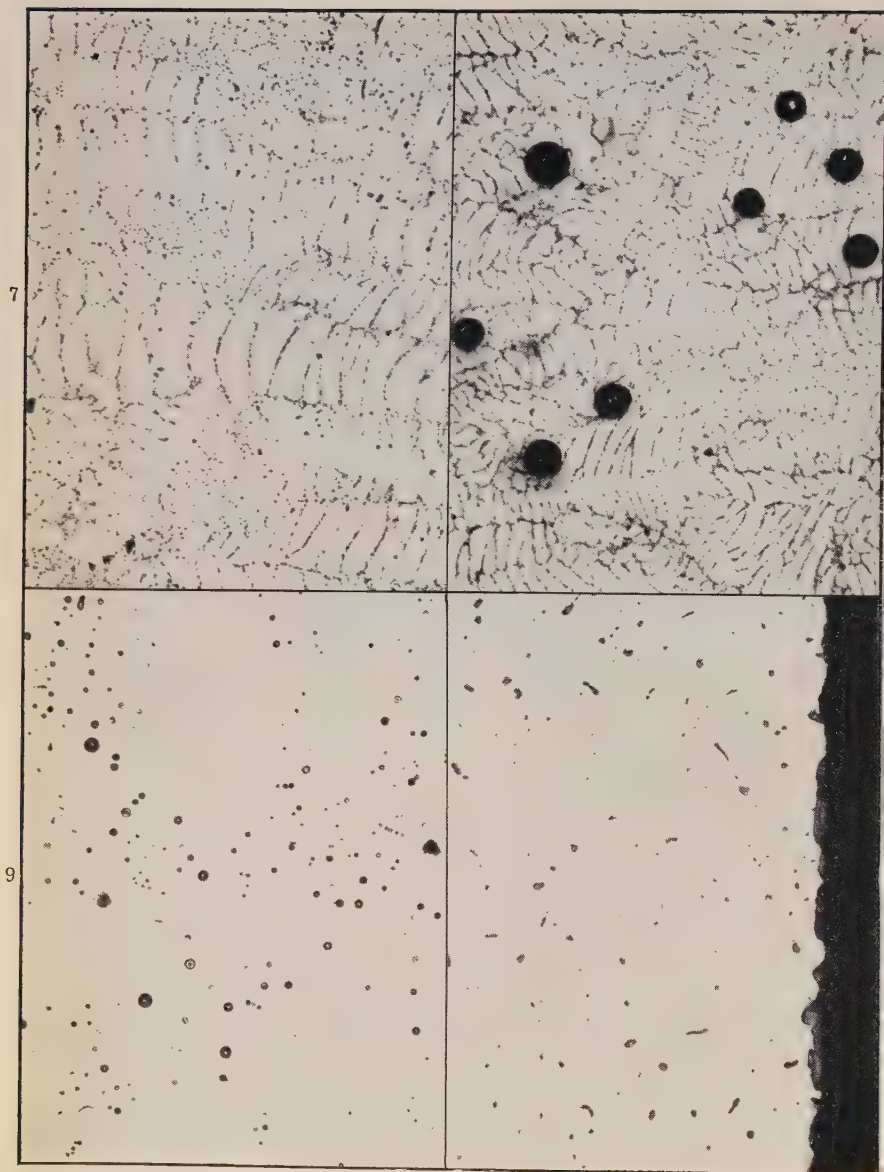


FIG. 7.—0.14% Sodium Alloy, cooled rapidly. Electrolytically polished and slightly etched in H.F. $\times 250$.

FIG. 8.—0.25% Sodium Alloy, cooled rapidly. Electrolytically polished and slightly etched in HF. $\times 250$.

FIG. 9.—Super-Purity Metal saturated with sodium at 700°C . and slowly cooled. Electrolytically polished and slightly etched in HF. $\times 250$.

FIG. 10.—Commercial-Purity Metal (0.23% Si, 0.47% Fe) heated in sodium for 501 hr. at 550°C . Unetched. $\times 200$.

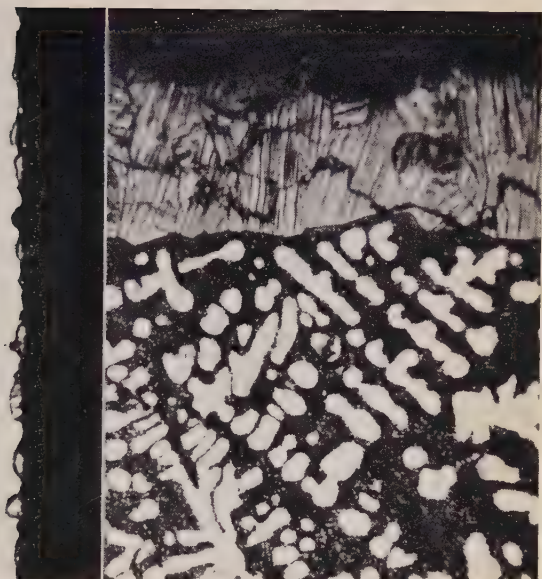


FIG. 11.—Super-Purity-Base Alloy (0.27% Si, 0.004% Fe) heated in sodium for 501 hr. at 550° C. Unetched. $\times 200$.

FIG. 13.—12.0% Silicon Alloy heated in sodium for 1 hr. at 700° C. and quenched. Etched in HF. $\times 300$.



FIG. 12.—11.0% Silicon Alloy heated in sodium for 60 hr. at 550° C. Unetched. $\times 200$.

crucible absorbed a certain amount of sodium and tended to disintegrate during the extraction, but free sodium was found to be always present at the end of the experiments. The ingots obtained were fairly sound, except for some shrinkage cavities at the top. They were trimmed

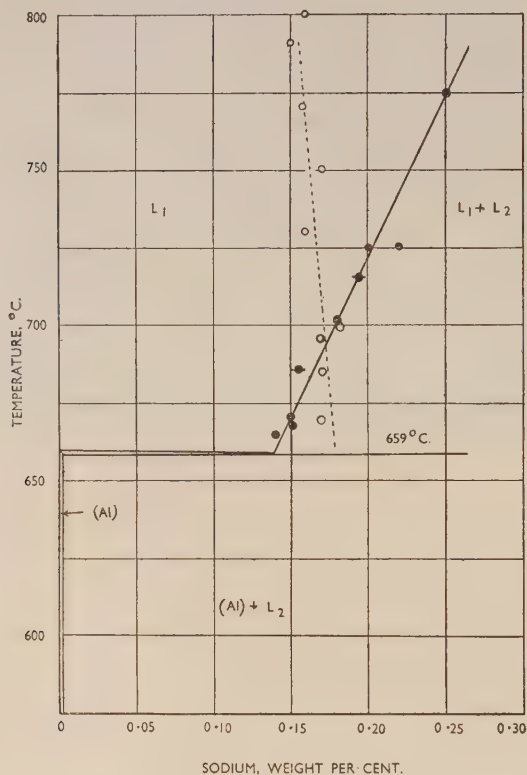


FIG. 3.—Aluminium-Sodium System.

KEY.

- Super-purity aluminium.
- Commercial-purity aluminium.
- Determinations by Fink, Willey, and Stumpf.²

up on a lathe, thoroughly pickled in dilute hydrochloric acid, and their densities determined (to ensure that blow-holes were absent) before submission for chemical analysis.

The sodium contents were determined by the analytical procedure outlined in Section II. The results obtained are summarized in Table II.

These results and those of Fink, Willey, and Stumpf² are plotted

in Figs. 3 and 4. Accepting the monotectic temperature (659°C.) given by these authors, the monotectic composition was found to be 0.14% instead of 0.18% sodium. This new value is still consistent with the solidus-liquidus points which they determined by thermal analysis, as is evident from Fig. 4 in which their actual experimental points are plotted. The main discrepancy is that the solubility was found to

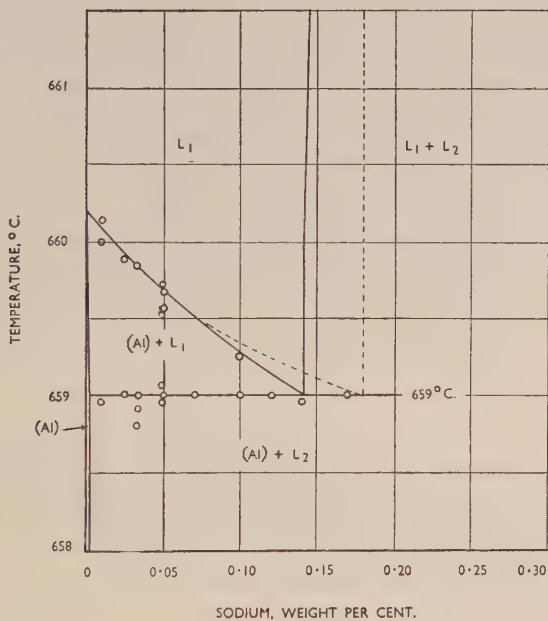


FIG. 4.—Aluminium-Sodium System : Monotectic Horizontal and Hypo-Monotectic Liquidus.

KEY.

- ○ -- Thermal data by Fink, Willey, and Stumpf.*
 ————— To accord with present work.

increase regularly with temperature and not, as in their results, to decrease; it is believed that the reason for this difference is that the rate of quenching in their experiments was probably not quite rapid enough to retain all the dissolved sodium in the ingot, and a comparison of the structures now obtained with the photomicrographs given in the American paper supports this view.

Fig. 7 (Plate XIV) shows the structure of the super-purity-base ingot obtained from a determination at 665°C. ; the herring-bone appearance of the monotectic is similar to that frequently observed in

eutectics crystallizing from very dilute solutions. Fig. 8 (Plate XIV) is a photomicrograph of the ingot quenched from 775° C. and shows the expected excess sodium constituent in globular form, together with monotectic. When an alloy of monotectic or hyper-monotectic composition was cooled fairly slowly, however, a coarse spheroidized structure was obtained instead of the herring-bone structure; this is illustrated by Fig. 9 (Plate XIV) which shows a super-purity sample cooled slowly from 700° C. The photomicrographs in the paper by Fink and his co-workers show a tendency to this type of structure.

The results given above call for little comment, but one point may be mentioned. The Le Chatelier equation may be used ² to check the solubility limits which have been determined. This relation is:

$$\text{Log}_{10} \frac{N'}{N} = \frac{H}{4.58} \left(\frac{1}{T} - \frac{1}{T'} \right) \quad . \quad . \quad . \quad (5)$$

where N' is the atomic fraction of solvent in the solid, N the fraction in the liquid phase, both in equilibrium at the monotectic temperature T (°K.). T' is the melting point of pure aluminium (933.3° K.) and H is its heat of solidification (2511 cal./g.-atom).

Taking the solid solubility as 0.002% sodium and the monotectic temperature as 659° C., the calculated value of the monotectic sodium content becomes 0.15%, in good agreement with the experimental figure of 0.14% obtained by the present authors.

IV.—EFFECT OF SILICON ON SOLID-SOLUBILITY LIMITS.

Some solid-solubility measurements were carried out in which commercial-purity aluminium was used instead of super-purity metal, and some rather remarkable results were obtained which led to a fuller investigation into the effect of silicon on the solubility limits.

It was found that when commercial sheet was heated in sodium at 550° C. for a prolonged period, it underwent a very pronounced diminution in silicon content; the iron content was not affected in any way. A similar fall in silicon content was then found to occur in super-purity base alloys of varying silicon and low iron contents. A micrographic examination of the sheets as extracted from the bomb with alcohol, showed that light grey crystals of a new phase were being formed at the surface of the metal. Characteristic examples of the effect in commercial aluminium and a super-purity-base silicon alloy are shown in Figs. 10 (Plate XIV) and 11 (Plate XV). This precipitate would, of course, be etched away in the deep pickle in acid which constituted the normal method of preparing samples for sodium analysis. The new phase thus formed is thought to be identical with that noted by Gwyer and Phillips ⁷ as occurring in aluminium-silicon alloys treated

with a considerable excess of sodium. Nowotny and Scheil in a recent paper ⁸ have also identified a ternary compound for which they give the X-ray diffraction pattern and to which they ascribe the formula NaAlSi_4 ; it is believed that the compound to which they refer is the same as that formed in the present experiments, but it has not been possible to confirm the composition which they put forward. Such evidence as is available indicates that the compound is probably based on the formula $\text{NaAlSi}_{1.25}$, but this point is discussed more fully later. For convenience the compound will be referred to subsequently as $[\text{NaAlSi}]$.

Scheuer, in a review ⁹ of the various theories which have been put forward to account for the modification phenomenon in silicon alloys, quotes some unpublished work by Czochralski on the diffusion of sodium into Alpac at temperatures just below the solidus, in which the growth of light-grey crystals inwards from the surface was noted. Czochralski has thus apparently carried out some experiments along somewhat similar lines to those now discussed, except that he used material with a high silicon content, whereas the present work is concerned mainly with percentages of silicon considerably less than 1%. As will be pointed out later, there is an important difference in the mechanism of the reaction with sodium in the two cases.

In order to investigate the effect more fully, a series of alloys was prepared from super-purity aluminium and a high-purity silicon hardener to give a range of silicon contents up to 0.27%. The iron contents were kept as low as possible. These materials were all chill-cast into slabs suitable for rolling and were rolled down to strip 1.5 mm. thick. Sodium-saturation experiments were then carried out by subjecting the samples to prolonged immersion in molten sodium in a bomb in the same way as in the earlier experiments on super-purity metal. After treatment they were deeply etched in hydrochloric acid and then analysed for sodium and silicon; in most cases the silicon was determined on the regulus remaining from the distillation for sodium.

The first tests were made at a constant temperature of 645° C. and were confined to alloys containing up to 0.10% silicon, since this was the maximum which could be used without any danger of exceeding the solidus. Also included in this series of tests were two new batches of super-purity metal which had rather lower silicon contents than the one previously investigated (J.R.1). The results obtained are summarized in Table III, which gives the original analyses of the materials and the final silicon and sodium contents which were found after treatment. The final iron contents are omitted, since in no case did these vary significantly from the percentage originally determined.

TABLE III.—*Effect of Silicon Content on Absorption of Sodium at 645° C.*

All specimens 1.5 mm. thick sheet.

Metal	Time of Heating, hr.	Original Analysis, wt.-%			Analysis after Treatment, wt.-%	
		Si	Fe	Na	Si	Na
Super-purity 445	332	0.0005	0.0005	0.0007	0.0005	0.0006
	670	0.0005	0.0005	0.0007	...	0.0012
Super-purity 3514	261	0.0008	0.0005	0.0008	...	0.0011
	670	0.0008	0.0005	0.0008	...	0.0031
Super-purity J.R.1	264	0.0025	0.0005	0.0002	...	0.0020
XA	163	0.0060	0.0010	0.0002	0.0055	0.0010
	337	0.0060	0.0010	0.0002	0.0045	0.0013
XB	167	0.0090	0.0010	<0.0005	0.0080	0.0022
ZN	330	0.015	0.0015	<0.0005	0.015	0.0022
ZO	330	0.03	0.0015	0.0005	0.03	0.0023
ZP	330	0.10	0.0015	<0.0005	0.10	0.0015

The analytical results given in Table III show that at this temperature there was no appreciable abstraction of silicon from the metal; the small decreases in the samples XA and XB are barely significant. No micrographic evidence could be found of compound formation, either at the surface or in the interior of the metal, and it was therefore concluded that a silicon content of up to 0.1% is stable under these conditions.

The final sodium figures show some deviations from the solubility values established at 645° C. for super-purity metal J.R.1 (Table I), but there is no systematic variation with silicon content, and no conclusions can be drawn as to the effect of silicon on the solubility of sodium in aluminium. It would require a good deal more work, which does not seem to be justified, to obtain any more accurate information on this point.

At lower saturation temperatures it was possible to use alloys with a silicon content higher than 0.10% and an additional alloy (ABW.1) containing silicon 0.27, iron 0.004, and sodium < 0.0005% was included in further tests which were carried out at 600°, 550°, and 500° C. At the last temperature 0.5 mm. strip was used instead of the normal

1.5 mm. material, so that a reasonable approach to equilibrium could be obtained without an excessive time of treatment.

The results obtained in these lower-temperature experiments are given in Table IV. The figures for iron content are again omitted.

TABLE IV.—*Effect of Silicon Content on Absorption of Sodium at 600°, 550°, and 500° C.*

Treatment in Sodium		Analysis, wt.-%					
Temperature, ° C.	Time, hr.	Alloy ZN		Alloy ZP		Alloy ABW.1	
		Si	Na	Si	Na	Si	Na
Untreated	...	0.015	<0.0005	0.10	<0.0005	0.27	<0.0005
600	504	0.10	0.0009	0.16	0.0008
550	475 501	0.015 ...	0.0009 ...	0.05 ...	0.0008 0.08	... 0.0016
500 *	461	0.03	0.0006	0.07	0.0014

* 0.5 mm. sheet was used for these tests, 1.5 mm. sheet for all the others.

The data are not as complete as could be wished, but the general trend is fairly clear: in certain samples the silicon was withdrawn from the metal and the composition of the alloy moved slowly to a silicon percentage which was constant for a given temperature. If the original silicon content of the metal was less than this equilibrium value it was not altered by the immersion in sodium (e.g. ZP at 600° C., ZN at 550° C.).

No precipitate of compound was visible on any of the microsections which were examined except on or very near to the surface of the metal; Fig. 11 (Plate XV) is typical of the type of structure obtained, except that in certain isolated cases an odd crystal of compound could be seen just inside the surface. The very low values found for the final sodium uptake, however, indicate that all traces of the compound must have been removed by the surface etch which was always carried out previous to analysis.

At temperatures below 600° C., the rate of diffusion of silicon in aluminium is more rapid than that of sodium: this is one reason why the compound is precipitated only at the surface of the specimens under these conditions. It is possible that the diffusion of sodium inwards is slowed down by the presence of silicon in solid solution in the aluminium. The relative concentrations of the two elements are also important

since the mechanism of the process is very similar to that observed in oxide sub-scale formation in copper alloys,¹⁰ in which it has been shown that the depth of oxide precipitation is an inverse function of the concentration of oxidizable element present in solid solution. In the present experiments, it is thus probable that the rate-controlling process in the establishment of equilibrium is the diffusion of silicon to the surface of the metal; for a given time of exposure to sodium, therefore, the fall in silicon content will be a certain *percentage* of the amount by which the initial silicon concentration exceeds the equilibrium value. Assuming that this is so, a simple calculation may be made from the results given in Table IV to obtain an estimate of the final silicon concentrations which would have been reached had the extractions gone to completion. By using the 550° and 500° C. results in this way, the equilibrium values obtained are as shown in Table V.

TABLE V.—*Estimated Final Silicon Concentrations.*

Temperature, ° C.	Final Silicon Concentration, wt.-%
645	>0.10
600	About 0.15
550	0.04
500	0.01

These figures then represent the silicon concentrations in the solid solution in equilibrium with liquid sodium and solid [NaAlSi] at the temperatures indicated. The data given in Table IV do not allow the corresponding equilibrium concentrations of sodium in solution to be stated precisely; all that can be said is that they probably lie within the limits 0.0016–0.0005%.

In any further experiments of this kind a more satisfactory procedure would be to establish the approximate equilibrium concentrations in the way described above and then to investigate the behaviour of a series of alloys in which the initial concentrations were increased in small steps within the appropriate composition range.

The Behaviour of High-Silicon Alloys.

One or two tests have been carried out on the reaction with sodium of alloys containing much higher percentages of silicon than in the experiments described above. The results are of interest since they demonstrate that a marked change in the diffusion mechanism occurs as the silicon content is increased. For example, Fig. 12 (Plate XV) shows a section through a 1-mm. thick sheet of 11% silicon alloy heated

in sodium at 550° C. for 60 hr. It will be seen that the compound has formed as long columnar crystals penetrating into the sheet and that those crystals reach almost to the zone of spheroidized silicon particles remaining down the centre of the metal. On continuing the heating to a total time of 200 hr., it was found that a microsection then showed only the light-grey second phase and no free silicon. The diffusion process in this case was thus much more rapid than in the corresponding experiments with low-silicon materials. A feasible explanation is that the rate of diffusion of sodium in $[\text{NaAlSi}]$ at a given temperature is probably much more rapid than the diffusion of silicon in aluminium, which has been indicated to be rate-controlling in the reaction at low silicon concentrations. If silicon is present, therefore, in sufficient quantity to enable large crystals of $[\text{NaAlSi}]$ to grow inwards from the surface, the aluminium between them will be denuded of silicon, and growth will take place mainly by deposition of compound at the tips of the advancing crystals.

This phenomenon has not been investigated in any detail, but one useful result was obtained from the experiments. By converting the silicon in a eutectic alloy completely to $[\text{NaAlSi}]$ by solid diffusion in this way, and then analysing the sheet for sodium and silicon, an estimate could be made of the Na : Si ratio in the compound. This was done on some sheet which had been treated at 525° C., and the following result was obtained as the mean of analyses on three separate samples : sodium 7.2, silicon 11.0 wt.-%. The Na : Si ratio obtained was thus 1 : 1.26 and differed very markedly from that in the formula NaAlSi_4 put forward by Nowotny and Scheil.⁸ Further evidence on this point is given in Section V.

V.—EFFECT OF SILICON ON LIQUID-SOLUBILITY LIMITS.

To complete the general survey of the solubility relationships in the binary and ternary systems, a further series of measurements was carried out in which alloys containing up to 16% silicon were heated with sodium at various temperatures (up to 700° C.) above their binary liquidus temperatures. For this purpose four alloys with nominal additions of 4, 8, 12, and 16% silicon were prepared from super-purity aluminium and a special hardener made from super-purity aluminium and acid-purified silicon powder. The sodium-bomb technique employed was similar to that already described in some detail in Section III.

It was noticed that the cylindrical samples of alloy, when extracted from the bomb after heating, had changed very little in dimensions, in spite of the fact that there was ample clearance in the graphite crucible

for the metal to melt down to a much larger diameter. Apart from some puckering at the tops of the cylinders, there was no external evidence of fusion. An explanation of this behaviour was soon apparent when sections were prepared for micro-examination. Fig. 13 (Plate XV), which is a photomicrograph of the edge of a cylinder containing about 12% silicon, quenched after treatment for 1 hr. at 700° C., illustrates a typical structure resulting from the immersion in sodium. A substantial and continuous skin was formed of a compound which appeared to be identical with that noted in the solid-diffusion experiments; the etching characteristics were similar, and micro-hardness measurements gave values of the same order in both cases. No signs of a duplex structure were found in the compound layer, and since there is no other evidence to suggest that more than one compound exists in the ternary system, it can be assumed that this is again the grey phase previously identified as $[\text{NaAlSi}]$.

A small amount of the compound was obtained in a moderately pure state by a procedure described later, and some tests were carried out to determine its approximate melting point. Samples of the crystals were heated to various temperatures in tiny air-tight steel capsules and then examined for evidence of fusion. It was found that decomposition occurred at 950° C. without any signs of melting at lower temperatures. The compound is thus quite stable and, under the conditions obtaining in the experiments just described, is formed as a rigid case which retains the molten cylinder of alloy. Once again, therefore, the measurements of the final concentrations of sodium and silicon present in the quenched alloys after removal of the outer skin (in this case by machining the cylinders), represent the concentrations of these elements in equilibrium with the compound at the temperatures concerned.

Two experiments were carried out on each alloy at each temperature, one in which a 1-hr. soak was given and the other in which this time was increased to 2 hr. The results of these determinations are given in Fig. 6 (Plate XIII), in which the percentages of sodium dissolved at 600°, 650°, and 700° C. have been plotted against the final silicon contents of the alloys. It will be seen that the determinations obtained after the 1 hr. and 2 hr. treatments are in reasonable concordance, indicating that approximate equilibrium was obtained in the shorter time of heating.

1. *The Ternary System.*

The curves which have been drawn through the experimental points in Fig. 6 (Plate XIII) represent the liquidus isothermals in the primary

field of the compound [NaAlSi], and it is pertinent to inspect the data now available to see to what extent the aluminium corner of this important ternary system can be sketched in.

The system clearly involves a ternary eutectic, in which the solids separating are aluminium solid solution, silicon, and [NaAlSi]. An estimate of the sodium content at the ternary eutectic point may be made as follows :

It can be seen from the data plotted in Fig. 6 (Plate XIII) that the solubility of [NaAlSi] in the melt is only slightly affected by variations in the silicon percentage when the latter is within the range 10–13%. This means that if a section of the ternary diagram is taken at a constant silicon content within these limits, the slope of the liquidus in the primary [NaAlSi] field will not differ appreciably from that in the parallel section containing the ternary eutectic point, if this also lies in this region. Actually the sodium content of the ternary eutectic must be very small, so that the percentage of silicon in it is unlikely to be very different from that in the binary eutectic (11.7%). It is thus permissible to draw the hypereutectic liquidus in a section for alloys containing approximately this amount of silicon, to extrapolate the curve to the ternary eutectic temperature, and so obtain the required sodium figure.

It was convenient to take for this purpose a section at approximately 11.0% silicon, since in addition to the three liquidus points read off from the curves in Fig. 6 (Plate XIII) some further results were available which could be plotted on the same curve. These were obtained in a separate series of experiments in which solubility measurements were carried out at different temperatures on a 2L.33 alloy of the following composition :

Si, %	Fe, %	Cu, %	Mn, %	Zn, %	Ni, %	Ti, %	P, %
11.65	0.23	0.006	0.003	0.01	0.004	0.015	0.00025

The final silicon content of this alloy, after treatment in sodium, varied from 10.5 to 11.5% in different experiments, but the solubility results obtained can be plotted at 11.0% silicon without important error. This has been done in Fig. 5. The three points for high-purity alloys containing this percentage of silicon, taken from Fig. 6, are also plotted, and it will be seen that the two sets of determinations are in very reasonable concordance. A smooth liquidus curve can therefore be drawn through them and extrapolated to lower temperatures. Alternatively, the results may be plotted on a logarithmic basis against the reciprocal of the absolute temperature; a straight line is then obtained which allows a more positive extrapolation to be made.

The freezing point of the ternary eutectic must now be considered.

There is no need to place this very accurately as far as the present estimation of the sodium content is concerned, since the probable error at the lower end of the solubility curve in Fig. 5 is quite large. The exact temperature is of considerable theoretical interest, however, because an adequate explanation of the modification process can only be given if the magnitude of the eutectic lowering produced by the sodium is known.

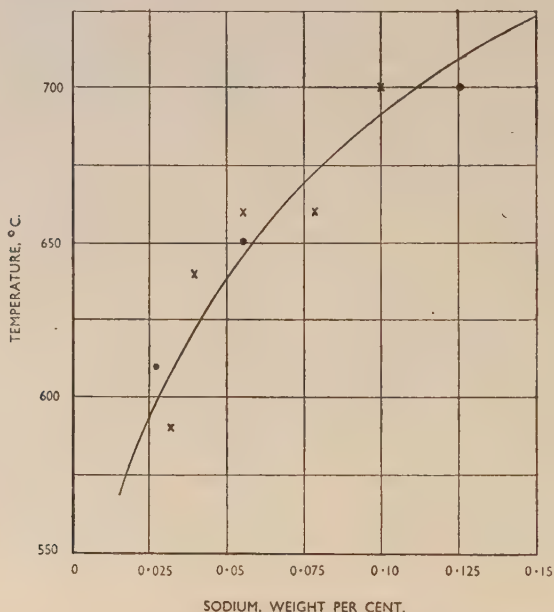


FIG. 5.—Aluminium-Silicon-Sodium System: Solubility Measurements at 11% Silicon.

KEY: ● Super-purity alloys; x Commercial base alloy.

No attempt has been made to determine the freezing point experimentally, since it is very doubtful whether equilibrium conditions can be achieved with this alloy either in freezing or melting. On theoretical grounds it is improbable that the ternary point will be more than 1° C. lower than the binary eutectic (577° C.); Scheil, in a recent paper,¹¹ calculates that 0.01 at.-% sodium will produce a depression of only 0.045° C. For practical purposes, therefore, the freezing point of the ternary eutectic may be taken to be the same as the binary eutectic, and on this assumption its sodium content, derived from Fig. 6, becomes 0.017%.

If then, in Fig. 6 (Plate XIII), the eutectic point *E* is placed at 11.7% silicon, 0.017% sodium, and 577° C., the ternary diagram as indicated by dotted lines appears to conform to the other data derived from the present experimental work. While it is not proposed to discuss in this paper the full implication of the suggested diagram with respect to the rather complex phenomena of modification, it should be pointed out that the percentage of sodium required for full modification of the binary eutectic alloy corresponds very closely to that given above for the ternary eutectic composition. It cannot be argued, however, that the finely dispersed structure obtained in the treated alloy is the natural consequence of ternary eutectic formation. There is no doubt that marked undercooling also occurs in these alloys at normal rates of cooling, and that this effect must be taken into account as well. In fact, the "protective colloid" theory put forward by Gwyer and Phillips⁷ still appears to provide an adequate explanation of the general mechanism of modification, if it is now assumed that the compound [NaAlSi] functions as the agent which hinders the crystallization of the silicon.

This compound, when primary, tends to separate as large plates; its characteristic appearance is illustrated in Fig. 14 (Plate XVI), which shows the structure of an alloy containing 11.0% silicon saturated with sodium by heating for 1 hr. at 850° C. and slowly cooled.

2. The Composition of the Ternary Compound.

To refer again briefly to the question of the composition of the ternary compound, Nowotny and Scheil⁸ prepared what they considered to be pure crystals of NaAlSi₄ by heating aluminium containing 50% silicon to 900° C. with excess sodium, allowing the melt to cool, and then extracting the compound by dissolution of the matrix alloy in amyl alcohol. The present authors have repeated this procedure very closely, except that the mix was heated to a temperature of 950°–1000° C. The blue plates extracted from the melt were ground under amyl alcohol and examined by X-ray diffraction.* The pattern obtained agreed very well with that given by Nowotny and Scheil for NaAlSi₄, but a subsequent chemical analysis gave the ratio of aluminium : sodium : silicon as 1.09 : 1 : 1.36. The sodium : silicon ratio previously found in the solid-diffusion experiments was thus confirmed, and suggests a formula based on NaAlSi_{1.25} or NaAlSi_{1.33}.

It is probable that the crystals analysed by Nowotny and Scheil were heavily contaminated with silicon, which was also present to some

* Mr. N. S. Brommelle, B.A., formerly on the staff of these Laboratories, kindly carried out this determination.

extent in the sample now used. The 50% silicon alloy from which the crystals were prepared could not be polished sufficiently well to photograph, but Fig. 15 (Plate XVI), which shows a 17.8% silicon alloy treated with sodium at 900° C., illustrates how massive silicon attaches itself to the plates of compound, making proper separation of the two phases extremely difficult.

The compound has a tetragonal crystal structure, and the lattice dimensions given by Nowotny are $a = 4.13$ and $c = 7.40$ Å. This gives a spacing along the [110] diagonal of 5.82 Å., which is sufficiently close to the normal lattice parameter in silicon ($a = 5.42$ Å.) to make continuous crystallization from one phase to the other feasible in a common [100] direction.

A note may be given on the behaviour of the grey phase during the preparation of micro-sections. It appears to be very readily attacked by moisture, and presentable sections can only be prepared by carefully avoiding all contact with water during polishing. On the other hand, the compound behaves in an extraordinarily inert manner in some circumstances, for example in acid solutions. This inertness seems to be due to a leaching-out of sodium from the surface layers, and as a result the compound then becomes comparatively non-reactive, even to water; it behaves, in fact, very much like silicon except that it is much softer. A slight scratch through the surface, however, is sufficient to start a vigorous corrosion going again. These observations confirm the general comments made by Gwyer and Phillips in their early paper.⁷

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“WHITE RUST” FORMATION ON ZINC.* 1269

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

The conditions under which zinc corrodes in moist atmospheres with the formation of a voluminous white corrosion product known as “white rust” were investigated. In unpolluted air of 100% relative humidity zinc was only tarnished, but white rust was rapidly produced when specimens were wetted with distilled water and kept in a humid atmosphere. The corrosion product usually consisted of basic zinc carbonate, but this was sometimes mixed with zinc oxide, and in the absence of carbon dioxide zinc oxide only was detected. The rate of corrosion was not altered by removing carbon dioxide from the atmosphere, and it is concluded that the primary reaction is the formation of zinc hydroxide precipitated at the meeting place of zinc ions and hydroxyl ions formed by electrochemical action. The rate of corrosion increased considerably when polluting substances such as sulphur dioxide, hydrochloric acid, or organic acids were present in the atmosphere, or when galvanizing-flux residues remained on the zinc surface. The rate of attack decreased in the presence of ammonia or high concentrations of carbon dioxide.

Precautions necessary to avoid white rusting in storage or transit are discussed. Simple immersion treatments in dilute chromate solutions are shown to give considerable protection, as did quenching in similar solutions after galvanizing.

I.—INTRODUCTION.

ZINC and zinc-coated goods sometimes develop a voluminous white corrosion product known as “white rust” during storage or transit, and this corrosion may be serious enough to render the goods unsaleable or, in the worst cases, to destroy the zinc coating entirely at some points. White rusting can cause serious disfiguration within a few days, and the investigation described in this paper is concerned with this rapid type of attack and not with the corrosion of zinc over long periods of exposure.

Published work on the subject is not extensive, but several

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papers ^{1, 2, 3, 4} show that white rust is likely to appear when zinc is exposed in damp, badly-ventilated places where condensation can readily occur. The corrosion product is said to be usually basic zinc carbonate or zinc oxide, or a mixture of the two.^{5, 6} Morral ⁵ does not agree with the view of Peirce ⁷ that zinc hydroxide is formed during white rusting.

The present research was undertaken to elucidate the mechanism of white rust formation, and the conditions under which it occurs and the influence of a number of factors on the rate of formation has been investigated. Analyses of corrosion products formed in various circumstances have enabled the probable reactions to be deduced.

It is shown that simple chromating processes offer considerable promise for the reduction or elimination of the white rusting which is liable to occur during the early periods of exposure of zinc-coated articles.

II.—MATERIALS USED.

Pure zinc sheet, two batches of hot-dipped steel sheet, and several samples of hot-dipped or electroplated steel wire, all commercially produced, were used for the tests. Details of these materials are given in Table I. In addition, specimens hot-dipped in the laboratory have been tested. These were prepared by dipping steel plates for 1 min. at 450° C., employing pure zinc baths, baths containing lead, and pure zinc baths to which 0.05, 0.1, or 0.15% aluminium had been added.

Unless otherwise stated, specimens with commercially-produced coatings were cleaned with calcium hydroxide paste, washed, and degreased with acetone before exposing; others were degreased with acetone only. Specimens cut from sheet were usually 5 cm. square, and wire specimens 3 in. long. Bundles or coils of wire weighing up to 14 lb. have also been used.

TABLE I.—*Details of Commercial Materials Used.*

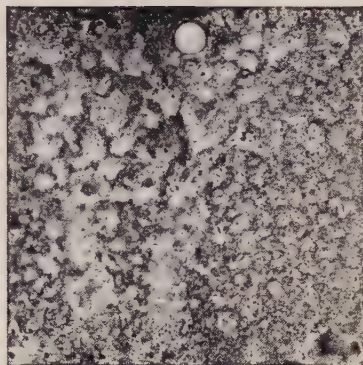
Material	Mark	Coating		S.W.G.	Impurity Content (spectrographic analysis)				
		Type	Approx. Thickness, oz./ft. ²		Pb, %	Cd, %	Al, %	Cu, %	Sn, %
Pure zinc sheet .	LYJ	15	0.002	0.002	n.d.	0.0005	n.d.
Sheet .	MLF	Hot dipped	0.9	21	1.0	0.2	0.001	0.01	0.02
Sheet .	NRG	Hot dipped	0.6	21	0.5	0.05	0.02	0.05	0.05
Wire .	OAJ	Electrodeposited	0.4	15	0.1	0.04	<0.002	0.02	<0.002
Wire .	OAH	Hot dipped	0.45	15	0.6	0.05	<0.002	0.02	<0.002
Wire .	OAA	Electrodeposited	1.5	11	0.01	0.02	0.002	0.01	<0.002
Wire .	NS5	Hot dipped	0.3	19	present	present	n.d.	n.d.	n.d.

n.d. = not detected.



FIG. 1.—Corrosion in Distilled-Water-Spray Test (MLF Galvanized Sheet).

(a) Uncorroded.



(b) Sprayed with distilled water twice daily and exposed for 1 week in 100% R.H. atmosphere.

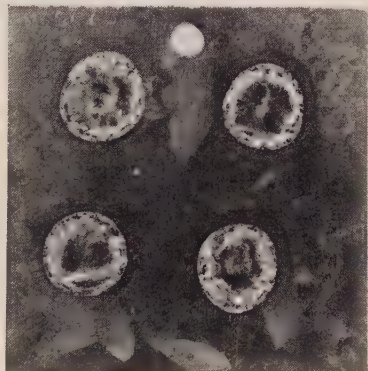
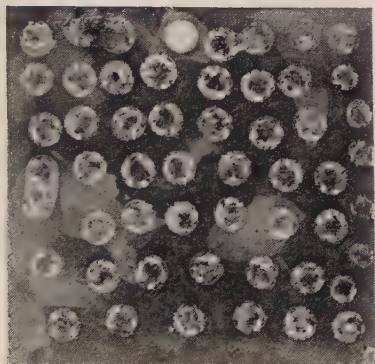


FIG. 2.—Corrosion by Pools of Distilled Water. Appearance of pools after 1 week in 100% R.H. atmosphere and subsequent drying.

(a) Pools consisting of 1 drop.

(b) Pools consisting of 16 drops.

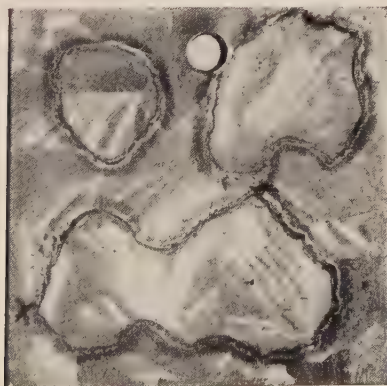


FIG. 3.—Corrosion at Perimeter of Squashed Water Drops. 2 days' test in 100% R.H. atmosphere.

III.—EXPERIMENTAL PROCEDURE.

In the majority of the tests specimens were exposed in glass tanks $13 \times 9 \times 8$ in. covered with a sheet of glass and containing $1\frac{1}{2}$ l. of distilled water so that the relative humidity (R.H.) was maintained at approximately 100%. For a number of experiments the specimens were sprayed for about 3 sec. twice daily with a fine spray of distilled water or some dilute solution. In some cases various dilute solutions were placed in the tanks instead of distilled water.

The exposure time was in most cases 7 days. After exposure the specimens were dried in air, and weighed, and then cleaned of corrosion product and weighed again. Corrosion products were removed by brushing with a bristle brush and by cathodic cleaning for 45 sec. in 10% potassium cyanide solution using a c.d. of 0.02 amp./cm.² It was confirmed that losses caused by these cleaning treatments were negligible.

As the amount of corrosion caused by 1 week's distilled-water-spray test varies to some extent owing to variations in spraying technique, atmospheric temperature, &c., controls were included each time the spray test was used.

IV.—WHITE RUSTING PRODUCED BY DISTILLED WATER.

1. *Exposure in Humid Atmosphere.*

Zinc or zinc-coated sheets, or small bundles of galvanized wire, exposed for 1 week in glass tanks in which the R.H. was 100%, were tarnished only. With the usual fluctuations of temperature in the laboratory only slight condensation occurred on the specimens, no large amounts of corrosion product were formed, and it was concluded that under these conditions true white rusting did not occur.

Considerable corrosion occurred within a few hours, however, when drops of water were placed on the zinc surfaces.

2. *Corrosion Produced by Condensed Water.*

Various methods of producing condensed water on the specimens in 100% R.H. tanks were tried, including:

- (i) Cooling the whole 100% R.H. tank below room temperature.
- (ii) Cooling the specimens themselves in the tank by placing them over dishes containing ice.
- (iii) Passing cold supply water through a galvanized pipe which was itself in a 100% R.H. vessel at room temperature.

Methods (ii) and (iii), but not method (i), produced large droplets of condensed water on the specimens owing to their being cooler than the surrounding atmosphere. Experiments by method (ii) showed that

about 0.017 oz./ft.² of zinc was corroded from galvanized sheet (material MLF) in 5 days, but after longer times the rate of attack fell off. Tests by method (iii) gave total losses of about 0.065 oz./ft.² in 1 week. Losses of this order (5–10% of a normal coating) would in practice produce large amounts of corrosion product, and render an article unsaleable.

3. Corrosion by Distilled-Water Spray.

Spraying with distilled water was found to be a convenient way of imitating the effects of condensation (see Fig. 1, Plate XVII). Sheets

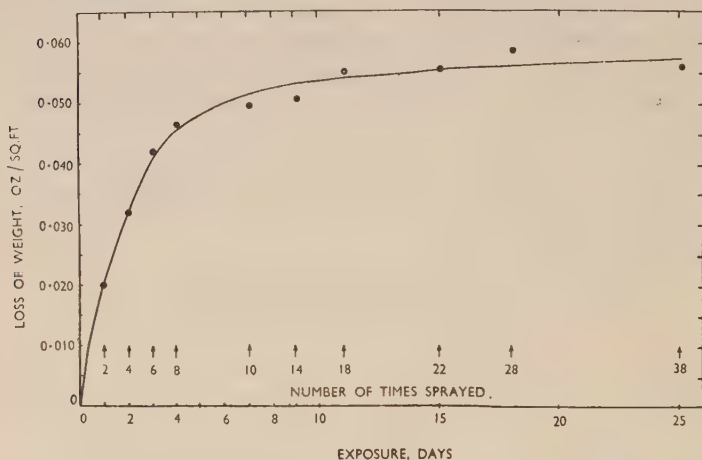


FIG. 4.—Loss of Weight for Various Times of Exposure of Galvanized Sheet Subjected to Distilled-Water-Spray Test. (Each point represents average loss for 2 sheets.)

or bundles of wire were suspended vertically in 100% R.H. tanks and sprayed twice daily for about 3 sec. with a fine distilled-water spray. This initially produced numerous small water droplets on the specimen surfaces, but later in the test these tended to run together. In one experiment hot-dipped sheets (material MLF) so treated lost an average of 0.042 oz./ft.² in a week. The attack was to some extent localized, and there were numerous points of penetration to the alloy layer.

Sheets similarly sprayed but exposed in the laboratory atmosphere (R.H. 50–70%) instead of being kept in a 100% R.H. tank, lost only 0.002 oz./ft.² in 1 week. These latter specimens did not exhibit white rusting, but tarnished only, and were no more corroded than specimens left in the 100% R.H. tank for a week without spraying. Specimens which were alternately wetted and dried by removing them from the

100% R.H. tank to the laboratory atmosphere for two 3-hr. periods each day during the spray test were corroded about 50% less than those kept in the 100% R.H. tank continuously.

The average attack on bundles of fifty 19 S.W.G. galvanized wires (material NSS) was about one-third to one-quarter as much as on single sheets in the spray test. This was because white rusting occurred on the outside of the bundles only, wires in the interior being practically unattacked. More attack could be produced on bundles of wire by dipping them in distilled water twice a day and keeping them in a 100% R.H. tank. The average loss in one such experiment was 0.027 oz./ft.², the wires in the interior being corroded to about the same extent as those on the outside of the bundle.

By exposing specimens to the distilled-water-spray test for various periods up to 25 days, it was found that the rate of white rusting fell off with time (see Fig. 4).

4. Effect of Method of Deposition of Water.

(a) Effect of Variation of Drop Size.

On each of two galvanized sheets (material NRG), laid horizontally in a 100% R.H. tank, were placed 54 separate pools of water, each consisting of a single drop from a burette fitted with a fine jet and delivering 75 drops/c.c. The total volume of water was thus 54/75 c.c. On each of two other specimens were placed 32 separate pools, each containing two drops from the burette, and on other duplicate specimens were placed 16, 8, and 4 pools each containing 4, 8, and 16 drops from the burette, respectively. Thus the same total volume of water (64/75 c.c.) was placed on each specimen, with the exception of those with the smallest pools, where there was not room to deposit 64 drops. The specimens were exposed in the 100% R.H. tank for 1 week.

There was a tendency for the attack to occur as a band of localized pitting round the perimeter of the pools; with the smaller pools the attacked area covered a greater proportion of the area of the pool than with the larger pools. This effect can be seen in Fig. 2 (Plate XVII), which shows two of the specimens after drying at the end of the test.

The total amount of attack produced by the pools (having corrected by the use of control specimens for the attack by humid atmosphere on areas not covered by pools) is plotted against the number of pools on the specimen, in Fig. 5.*

The results show that :

(i) The total attack by a fixed volume of water rises as the water is

* The figures for the sheets with the smallest pools are adjusted to correspond to 64 drops instead of 54, so that the volume of water is the same for each specimen.

divided into an increasing number of separate pools, but the relationship is not linear and there appears to be a limiting value above which further sub-division would not cause further increase of attack (see Fig. 5).

(ii) For the smaller pools the attack produced by a single pool is approximately proportional to the area covered by the pool (see Fig. 6). This is in agreement with the observation that most of the area covered by the pool was corroded in the case of the smaller pools.

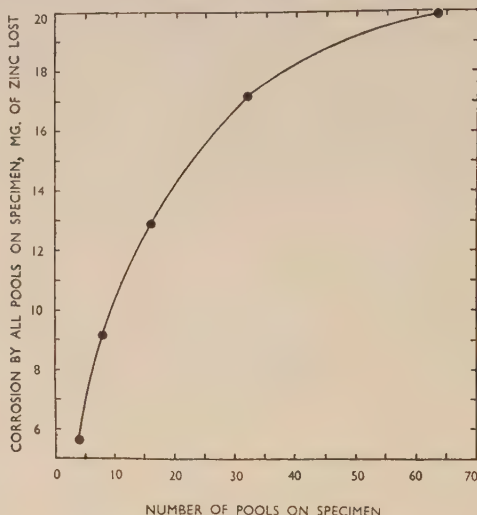


FIG. 5.—Total Corrosion Caused by Equal Quantities of Distilled Water Distributed on Galvanized Sheets as Various Numbers of Pools. Total volume of water on each sheet = 64/75 c.c. 1 week's test.

For the larger pools the attack produced by a single pool is not proportional to the area covered by the pool (Fig. 6), and there is an indication that for even larger pools the attack would become approximately proportional to the length of the perimeter. This is to be expected, since most of the attack occurs round the perimeter in the case of the larger pools.

These results are discussed in Section VIII.

(b) *Effect of Movement of Corroding Water.*

It was considered that the corrosive effects of stagnant thin films of water might differ from those of moving films such as occur when goods are exposed to rain. Specimens dipped in distilled water and then placed in a 100% R.H. tank were therefore compared with specimens sprayed continuously with distilled water. It was found in two tests

that the amount of corrosion produced was approximately the same whether the film was moving or stagnant. In both cases the corrosion was rather more than on similar specimens totally and continuously immersed in distilled water. No detailed examination of this problem could be undertaken, however.

(c) *Attack in Interior of Stacks of Sheets or Coils of Wire.*

In a number of experiments no intense attack was produced in the interior of stacks of sheets or bundles of wire. When such stacks or bundles were sprayed with distilled water little penetration into the interior occurred and only the outermost sheets or wires showed severe white rusting. This also applied to large bundles of wires which were cooled and then placed in a 100% R.H. tank at room temperature to produce condensation. For example a 14 lb. bundle (material OAH) bent into a circle was hung for a week in a 100% R.H. tank. (Such large bundles were exposed as received from the makers, without calcium hydroxide cleaning or degreasing.) This bundle was removed four times during the week and cooled, the average amount of cooling being 17° C. below the temperature of the tank. Considerable condensation occurred on replacing the bundle after each cooling, but after a week the wires in the interior were only tarnished. The outside wires were extensively coated with white rust, and the bundle was in an unsaleable condition after the test. The total weight of corrosion product formed was about 4 g.

A 14 lb. bundle (material OAH) was exposed on the laboratory roof for 2 months, during which time 2.3 in. of rain fell. After exposure the wires in the interior were severely tarnished, but there was no white rust inside the bundle.

A 14 lb. coil of 14 S.W.G. electroplated wire was twice dipped into distilled water with intermediate knocking and shaking to ensure that water penetrated into the interior. After the excess water had been

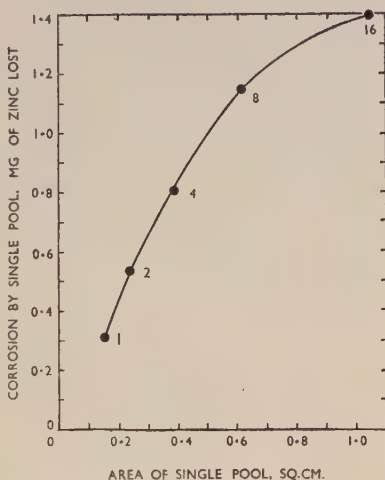


FIG. 6.—Corrosion of Galvanized Sheet by Distilled-Water Pools of Various Sizes. Number of drops in pool given against each point. 1 week's test.

drained off it was found that 48 g. of water were retained. The coil was then laid horizontally in a large 100% R.H. tank; after 4 days it was removed and dried. In this case the coil showed severe white rust attack, both inside and outside, and considerable amounts (about 13 g.) of loose white corrosion product were formed.

It therefore appears that pure water will only cause white rusting in the interior of coils of wire when considerable amounts of water are able to penetrate the outer layers and are prevented from evaporating. In this case the amount of attack is probably governed by the accessibility of oxygen. This is illustrated by Fig. 3 (Plate XVII), which shows attack confined to the perimeter of squashed drops in a test where drops were placed between galvanized sheets in a pile.

5. *Effect of Carbon Dioxide.*

Galvanized specimens (material NRG) were hung for a week in 100% R.H. tanks through which ordinary air, CO₂-free air, and air containing 1.5% CO₂, respectively, were continuously passed. The specimens were sprayed twice daily with water saturated with the corresponding gaseous mixture. The losses of weight resulting are given in Table II. These results show that the carbon dioxide present in the atmosphere does not accelerate the white rusting process. In fact when relatively large amounts of carbon dioxide are present the rate of attack is considerably reduced.

TABLE II.—*Effect of CO₂ on Rate of White Rusting in Distilled-Water-Spray Test.*

Specimen No.	Atmosphere	Loss of Weight, oz./ft. ²
305 309 312	Ordinary air	0.043 0.040 0.045
306 310 313	CO ₂ -free air	0.040 0.043 0.046
307 308 311	Air containing 1.5% CO ₂	0.016 0.018 0.016

V.—EFFECT OF VARIOUS IMPURITIES IN THE ENVIRONMENT.

1. *Dilute Mineral Acids.*

Rain-water in industrial districts may have a pH as low as 3.0 owing to the presence of sulphur dioxide, sulphur trioxide, and hydro-

chloric acid in the atmosphere. Experiments were carried out to determine whether white rusting is accelerated under such conditions. Specimens were subjected to the spray test using (a) distilled water, (b) sulphuric acid solution of pH 4, and (c) hydrochloric acid solution of pH 4. Losses of 0.05–0.06 oz./ft.² were produced after 1 week, the solutions of sulphuric or hydrochloric acids of pH 4 causing only about 10% more attack than distilled water.

Since zinc chloride is deliquescent and becomes wet at relative humidities greater than about 10%, the formation of zinc chloride on zinc surfaces might be expected to cause severe attack. Severe attack did in fact occur when zinc chloride was placed on galvanized specimens (see Section V. 3). Other experiments have shown, however, that by the action of dilute hydrochloric acid solutions on zinc no appreciable amounts of deliquescent salt are formed. This may be because zinc chloride is readily hydrolysed to the relatively insoluble zinc oxychloride. Thus small pools of hydrochloric acid of pH 2, 3, and 4 placed on horizontal galvanized sheets in a tank with 85% R.H., all became dry after 3 days. After 1 week the specimens were removed to a 100% R.H. tank and left for 8 weeks, being weighed periodically. Graphs of gain in weight against time for the various specimens are shown in Fig. 7.

The dried pools attracted a little moisture, particularly those which were initially of pH 2, but in all cases the rate of attack fell off with time (as in the distilled-water-spray tests). Attack on specimens with pools

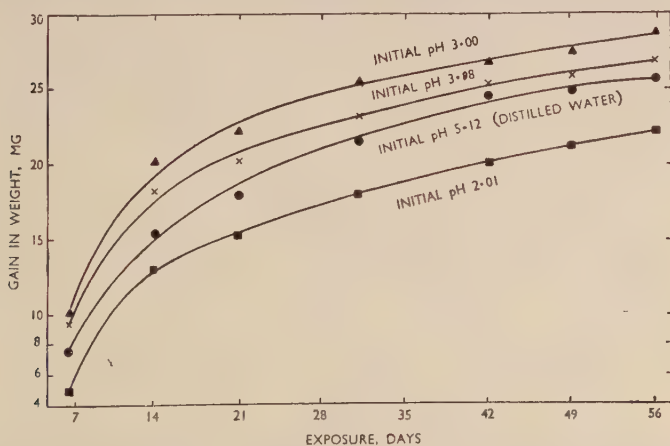


FIG. 7.—Gain in Weight, on Exposure in 100% R.H. Tank, of Galvanized Sheets on which Pools of Distilled Water or Dilute Hydrochloric Acid were Placed. Each specimen 5 × 5 cm., with 50 pools each approx. 0.5 cm. in dia.

of hydrochloric acid of pH 2 was found after the test to be less than attack on the other specimens, but no explanation of this is offered.

2. Hydrochloric Acid Vapour.

Two galvanized sheets (material NRG) and a bundle of 50 wires (material NSS) were hung in a tank containing 20% hydrochloric acid solution for 50 days and weighed periodically, the partial pressure of hydrogen chloride in the atmosphere being 0.2 mm. Hg. The specimens were severely attacked, and the rate of attack remained constant (Fig. 8), probably owing to the continuous supply of acid vapour to the specimens, but not to the formation of deliquescent zinc chloride since the thick white corrosion product was found to be largely zinc oxychloride. The amount of chloride in the corrosion product was negligible. It is interesting to note that even in this experiment there was practically no attack in the interior of the bundle of wires.

3. Chlorides and Flux Residues.

Small heaps (0.05 g.) of ammonium chloride, zinc chloride, or a mixture of the two, placed on horizontal galvanized sheets exposed in a 100% R.H. tank for 1 week, quickly attracted moisture and became pools of liquid. Severe attack was caused by these pools, the worst being by ammonium chloride alone. In this case the average attack over the pool area after a week was 0.19 oz./ft.² This demonstrates the danger of flux residues on galvanized surfaces.

Galvanized specimens sprayed twice daily with 3% sodium chloride

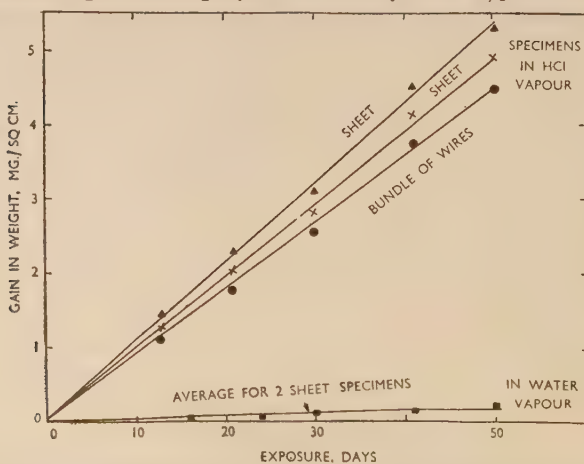


FIG. 8.—Gain in Weight of Galvanized Sheets and Wires Exposed to the Atmosphere over 20% Hydrochloric Acid.

solution and kept in a 100% R.H. tank for a week lost an average of 0.072 oz./ft.², as compared with 0.047 oz./ft.² lost by specimens sprayed with distilled water. Chloride therefore accelerates white rusting, though 3% sodium chloride solution caused only about 50% more attack than distilled water in the spray test.

4. Sulphur Dioxide.

Various amounts of a solution saturated with sulphur dioxide at 20° C. were added to 1½ l. of distilled water and placed in covered glass tanks. Galvanized sheets (material NRG) were exposed horizontally in the tanks for 1 week. The results are summarized in Table III.

Very severe corrosion occurred when 1.0 c.c. or more of saturated sulphur dioxide solution was added, but 0.25 c.c. or less appeared to have no effect. In the case of the most concentrated solution analysis showed that after 1 week about two-fifths of the sulphur dioxide initially present had reacted with the specimen, one-third remained in the tank almost entirely as sulphuric acid, and the remainder had presumably escaped.

X-ray analysis showed the corrosion products to consist largely of ZnSO₄.H₂O and ZnSO₄.6H₂O.

5. Formic Acid.

No appreciable increase in attack in the spray test occurred on galvanized sheets (material NRG) when a formic acid solution of pH 4 was used instead of distilled water (with the corresponding solution

TABLE III.—Effect of Moist SO₂ on Corrosion of Galvanized Steel.

Volume of Conc. SO ₂ Solution Added to Tank, c.c.	Odour in Tank Initially	Conditions of Specimens	Loss of Weight in 1 week, oz./ft. ² *
20	Strong	Large pools of liquid quickly appeared on surface	0.253 †
8	Strong	Large pools of liquid quickly appeared on surface	0.154
2	Easily detectable	Smaller pools of liquid quickly appeared on surface	0.064
1	Just detectable	Very fine droplets appeared on surface	0.030
0.25	Not detectable	Only a very little liquid detectable	0.005
0.1	Not detectable	No liquid observed on the surface	0.004 †
0	...	No liquid observed on the surface	0.005

* Average for both sides. Attack was most severe on the upper surfaces.

† Single experiment only. Otherwise mean of two results.

in the bottom of the 100% R.H. tanks). There was a slight increase in attack, however, when specimens were suspended over formic acid solution of pH 3.8 (without spraying), the loss of weight after a week being 0.006 oz./ft.² compared with 0.003 oz./ft.² for specimens in the ordinary 100% R.H. tank.

6. *Acetic Acid.*

Galvanized sheets (material NRG) were more heavily attacked in the spray test when sprayed with acetic acid solution of pH 3.8 than when sprayed with distilled water (with the corresponding solution in the bottom of the 100% R.H. tanks); the average loss caused by acetic acid was 0.065 oz./ft.² against 0.040 oz./ft.² by distilled water. X-ray analysis showed that the corrosion product was in both cases largely basic zinc carbonate.

A more marked difference was found, however, when specimens were suspended above acetic acid solution without spraying. Thus, the average loss for specimens hung above acetic acid solution of pH 3.8 for 1 week was 0.021 oz./ft.², while for specimens in the ordinary 100% R.H. tank the average loss was 0.005 oz./ft.²

7. *Ammonia.*

Galvanized sheets (5×5 cm.) placed horizontally for 1 week in tanks containing (a) distilled water and (b) a 0.1% solution of 0.880 ammonia, all gained about 6 mg. The specimens were then hung vertically in the same tanks and sprayed twice daily with distilled water for a further week. The average loss after the test for the specimens in the ammoniacal atmosphere was 0.022 oz./ft.², and for those in the ammonia-free atmosphere 0.035 oz./ft.² The corrosion product on the former specimens was found by X-ray analysis to consist mainly of basic zinc carbonate, with a small amount of zinc oxide.

Appreciably less attack occurred in the ammoniacal atmosphere, probably because the pH of the liquid on the zinc surfaces was raised.

8. *Insulating Materials.*

One of the causes of corrosion of cadmium plating in electrical equipment is the acid vapours given off from certain insulating tapes, in the presence of moisture. These acid vapours have also been found to accelerate considerably the white rusting of zinc, both at room temperature and at higher temperatures.

Thus, specimens (material NRG) hung in a 100% R.H. tank at room temperature lost 0.005 oz./ft.² in a fortnight, while specimens in a similar tank containing lengths of a sample of yellow Empire insulating tape lost 0.026 oz./ft.² Litmus paper in the tank or in the water at the

bottom of the tank turned red when the tape was present, and the pH of the water became as low as 3.5.

In another test galvanized specimens (material NRG) 2.2×5 cm. were suspended in 500 c.c. flasks which were plugged to give limited access to the atmosphere. Lengths of yellow insulating tape were placed in two of the flasks and two other flasks contained no tape; 0.24 c.c. of water was placed in each flask at the beginning of the test and a further 0.16 c.c. added during the test, which was of 12 days' duration, the temperature being maintained at 60° C. during 7 of these days. The specimens in the flasks containing water and tape lost 0.027 oz./ft.², and those in the flasks containing only water lost 0.004 oz./ft.²

The corrosion product formed on the galvanized specimens in the presence of the insulating tape was not identified completely, but zinc salts of the fatty acids (such as butyric acid) were found.

Other non-metallic components of electrical equipment are capable of accelerating the corrosion of zinc in moist conditions. Thus, in a test at 60° C. carried out in a similar manner to that described above (in this case 0.24 c.c. water was added at the beginning and at three other periods during the 7 days' test at 60° C.), galvanized specimens (material NRG) lost 0.021 oz./ft.² in the presence of pieces of a phenol-formaldehyde resin. In the presence of resin but with no water added the loss was 0.001 oz./ft.², while, as shown above, in the presence of water alone the loss is about 0.004 oz./ft.² In this case acid vapours are not responsible for the increased attack, since the resin evolves ammoniacal vapours at 60° C. Ammonia by itself would be expected to decrease the amount of attack (see Section V. 7), so presumably some accelerating agent is also evolved.

VI.—FACTORS CONNECTED WITH THE METAL.

1. Surface Roughness.

Galvanized sheet of material MLF was found to have one side considerably rougher than the other. Specimens, each with one side stopped-off, were exposed to the distilled-water-spray test. The loss of weight of the rough sides averaged 0.057 oz./ft.² in a week and that of the smooth sides 0.061 oz./ft.², from which it was concluded that the roughness had had very little effect on the rate of white rusting.

2. Surface Films.

(a) Effect of Different Surface Treatments.

Table IV shows the effect of different initial surface treatments on the white rusting of galvanized sheet (material MLF) in 1 week's distilled-water-spray test.

TABLE IV.—*Effect of Surface Preparation on Rate of White Rusting in Distilled-Water-Spray Test.*

Surface Treatment	Total Loss of Weight, oz./ft. ²
Degreased only	0.050 } 0.052 } Mean 0.053 0.056 }
Cleaned with Ca(OH) ₂ paste and degreased .	0.069 } 0.073 } Mean 0.071 0.072 }
Immersed 10 sec. in 2% H ₂ SO ₄ and degreased .	0.076 } 0.073 } Mean 0.075 0.076 }

After treatments which removed the oxide film there was about 40% more attack in the spray test. The film removed was that which was formed while the galvanized sheet cooled from the galvanizing temperature (about 450° C.) and during subsequent storage for about 4 years at room temperature.

(b) *Age of Galvanized Sheet.*

Since, as shown by the results in Table IV, the oxide film has a certain protective value, there appeared to be some basis for the belief that galvanized sheet is more prone to white rusting immediately after preparation than when it has been stored for some time. Specimens (6 × 7.5 cm.) galvanized in pure zinc baths (i) 18 months, and (ii) 2½ hr. before the test began were subjected to 1 week's distilled-water-spray test. The average losses were 0.015 oz./ft.² for the stored specimens and 0.017 oz./ft.² for the freshly-prepared specimens.

The freshly-prepared sheets were thus only very slightly more heavily attacked than the stored sheets. Hot-formed oxide films were present on all the specimens, but on the stored specimens the film was presumably thicker owing to growth at room temperature. In conjunction with the results on surface preparation (see Table IV) it therefore appears that the protection afforded is largely due to the hot-formed film. This is supported by the results given below of tests in which hot-dipped and electroplated wires were compared.

(c) *Different Types of Coating.*

Bundles of degreased wires were dipped twice daily in distilled water and suspended in a 100% R.H. tank for a week. Electroplated wires lost on the average 0.032 oz./ft.² (material OAJ) and 0.034 oz./ft.² (material OAA), while hot-dipped wires lost 0.024 oz./ft.² (material OAH).

The reasons why electroplated wires lost about 35% more than hot-dipped wires may have been:

(i) The oxide film on the hot-dipped wires is probably considerably thicker than that on the electroplated wires.

(ii) The compositions of the coatings and their physical states are different.

(iii) Penetration of hot-dipped coatings is interrupted when the alloy layer is reached.

During these tests it was shown that wires in the interior of the bundles were not corroded to a significantly different extent from those on the outside.

3. Effect of Impurities in Coating.

The above experiment showed that electroplated wire was about 35% more heavily attacked than hot-dipped wire (analyses in Table I). This is not, however, a good guide to the effect of impurities in the coating owing to variations in other factors.

(a) Lead.

Freshly-galvanized sheets (6×7.5 cm.) degreased with acetone were exposed to 1 week's distilled-water-spray test. Specimens prepared from a pure zinc bath lost 0.017 oz./ft.², and specimens from a bath containing 1.2% lead lost 0.021 oz./ft.², i.e. about 20% more. Lead in the galvanized coating thus appears to cause a slight decrease in resistance to white rusting.

(b) Aluminium.

Results of 1 week's distilled-water-spray test on sheets (2.3×4.3

TABLE V.—Corrosion of Hot-Dipped Coatings Containing Aluminium in Distilled-Water-Spray Test.

Aluminium Added to Bath,* %	Total Loss of Weight, oz./ft. ²
0	0.023 0.027
0.05	0.007 0.008
0.10	0.008 0.013
0.15	0.013 0.024

* The percentage of aluminium in hot-dipped coatings is usually about twice that in the bath over this range.

cm.) prepared from baths containing various amounts of aluminium are given in Table V. Aluminium considerably reduced the rate of white rust formation, the optimum addition to the galvanizing bath being about 0.05%. The galvanizing baths concerned contained no lead.

VII.—PROTECTION AGAINST WHITE RUSTING.

1. *Inhibitors.*

A proprietary vapour-phase inhibitor, which is effective in reducing the corrosion of steel in damp atmospheres, was found to be ineffective in the case of galvanized specimens.

2. *Chromate Treatment.*

It is known that chromating by dipping in strong acidified sodium dichromate solution (specification D.T.D. 923 *) affords very good protection to zinc. The results given in Table VI show that during 1 week's test almost complete protection is afforded against 100% R.H. with intermittent distilled water spray or 3% sodium chloride solution spray.

This process is too expensive for general application to galvanized goods and, moreover, the yellow colour produced is often objectionable, but it is used in special cases where high corrosion-resistance is essential. A less effective and temporary protection would, however, be sufficient to prevent the worst effects of white rusting.

A dip in 0.07% unacidified sodium dichromate solution at 65° C., which does not discolour the surface, was known to provide some protection. Specimens treated in this way received considerable protection against the effects of the distilled-water-spray test. The minimum time of dip necessary to give the optimum effect was found to be about 30 sec. (see Fig. 9), and dips of this duration or longer reduced the loss in weight by as much as 80% of the value for untreated specimens.

In the distilled-water-spray test specimens dipped in 0.07%

TABLE VI.—*Protection Afforded to Galvanized Sheet by Chromate Treatment to D.T.D. 923.*

Treatment of Galvanized Sheet	Total Loss of Weight in 1 Week, oz./ft. ²	
	Distilled Water Spray	3% NaCl Spray
None	0.047	0.072
Chromated to D.T.D. 923	0.002	0.003

* The chromating solution specified contains 200 g. sodium dichromate crystals and 6.6 c.c. conc. H₂SO₄ in 1 l. H₂O.

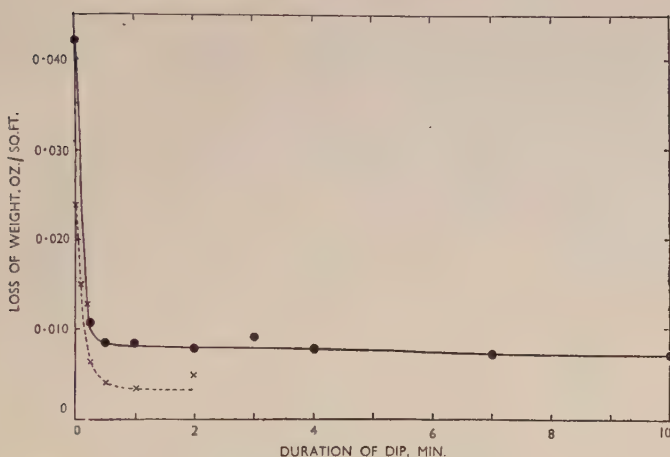


FIG. 9.—Effect of Dip in Sodium Dichromate on Corrosion of Galvanized Sheet in Distilled-Water-Spray Test. 1 week's test. (Different spraying nozzles used for the 2 tests.)

dichromate solution to which a wetting agent (Teepol) had been added, lost 20% more weight than specimens from the same solution without the wetting agent. Dipping at 75° C. instead of 65° C. caused no significant improvement, nor did the use of a 0.1% instead of a 0.07% solution.

To investigate the effects of solutions with a range of dichromate contents, specimens were dipped for 30 sec. in the following series of solutions :

(a) 0.07%—5% dichromate, unacidified, at 65° C.

(b) 0.07%—5% dichromate with H_2SO_4 in the same ratio as in D.T.D. 923, at 40° C.

(c) As (b), but at room temperature.

The results of these tests are given in Fig. 10, which shows that very good protection results from dipping in acidified 1% sodium dichromate solution for 30 sec. at room temperature or at 40° C. In all cases the sheets dipped in the 5% solutions were yellowish in colour; there was practically no colour on those dipped in the other solutions, except a slight coloration on those dipped in the acidified solutions at 40° C.

A series of specimens were dipped in 1% acidified dichromate solution at room temperature for various times and subjected to the distilled-water-spray test. The results are given in Fig. 11, which shows that 10–15 sec. dip is sufficient to give nearly the maximum protective effect.

In view of the promising results of these chromate treatments it was considered that it might be advantageous to quench galvanized

articles in dilute chromate solutions instead of in water. Accordingly, specimens were galvanized for 1 min. in a bath at 450° C. containing

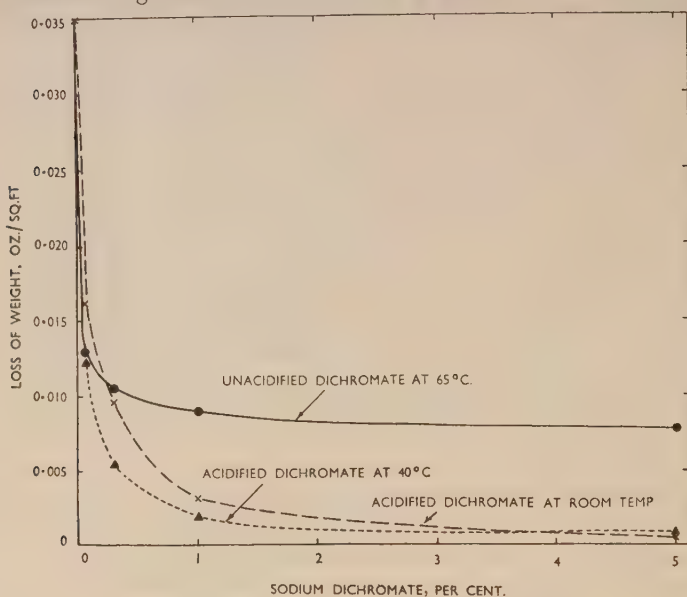


FIG. 10.—Protection Afforded by Various Chromate Treatments. $\frac{1}{2}$ -min. dip in all cases. 1 week's distilled-water-spray test.

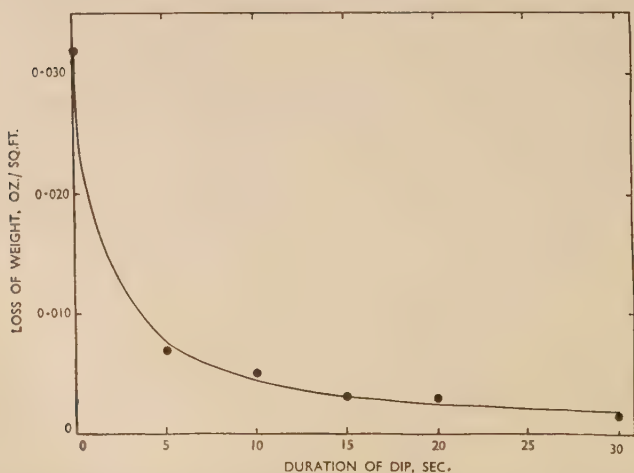


FIG. 11.—Effect of Dip in Acidified 1% Sodium Dichromate Solution on Corrosion of Galvanized Sheet in Distilled-Water-Spray Test. (Each point represents average loss for 2 specimens.) 1 week's test.

1% lead, by prefluxing in hot saturated ammonium chloride solution and scattering a little ammonium chloride on the bath during withdrawal. The specimens were quenched in (i) water, (ii) 0.07% unacidified sodium dichromate solution, or (iii) 1% acidified sodium dichromate solution, and held in the quenching baths (all at room temperature) for 5 sec. They were then dried with a cloth and subjected to 1 week's distilled-water-spray test. The behaviour of these specimens was compared with that of other specimens which were similarly galvanized, quenched in cold water, and subsequently dipped for 5 sec. in 0.07% unacidified dichromate solution at 65° C. or 1% acidified dichromate solution at 50° C. The results are given in Table VII.

These results show that good protection against white rust was given by quenching from the galvanizing bath into either 0.07% unacidified or 1% acidified dichromate solutions, both cold, even though the time of immersion was only 5 sec. The protection afforded was much better, especially with the weaker solution, than that afforded by quenching in cold water and subsequent immersion for 5 sec. in the corresponding hot chromating solutions.

If this method is to be of practical use the chromating solutions must not be adversely affected by the accumulation of flux residues in the quenching bath. Specimens were therefore chromated by immersion (a) for 30 sec. in 0.07% unacidified dichromate solution at 65° C., and (b) for 10 sec. in 1% acidified dichromate solution at 50° C., with and without 2% of added zinc ammonium chloride in each solution. The specimens were then subjected to a week's distilled-water-spray test. In neither case did the presence of the chloride flux residue adversely affect the protection afforded by the chromate treatments.

TABLE VII.—*Effect of Quenching in Dichromate Solutions on Corrosion in Distilled-Water-Spray Test.*

Specimen and Treatment	Loss of Weight after Test, oz./ft. ²
Galvanized and cold-water quenched	0.025 0.025
Galvanized and quenched in cold 0.07% unacidified dichromate solution	0.007 0.003
Galvanized and quenched in cold 1% acidified dichromate solution	0.002 0.002
Galvanized, cold-water quenched, and subsequently dipped 5 sec. in 0.07% unacidified dichromate solution	0.024 0.018
Galvanized, cold-water quenched, and subsequently dipped 5 sec. in 1% acidified dichromate solution	0.005 0.005

Further specimens were galvanized through a thick zinc ammonium chloride layer, quenched in cold water or in 0.07% unacidified or 1% acidified dichromate solutions, and hung up to drain. These were then exposed in a 100% R.H. tank for 3 months. The specimens which had been quenched in the dichromate solutions remained bright and suffered no serious attack, while those quenched in water tarnished quickly and showed fairly severe local attack after the test, probably at places where traces of flux residues remained.

Another series of distilled-water-spray tests showed that the protective effect of chromating (with 0.07% unacidified or 1% acidified solutions) was the same whether the specimens were rinsed after chromating or not. A disadvantage of omitting to rinse, however, is that the coatings retain yellow stains.

VIII.—MECHANISM OF WHITE RUST FORMATION.

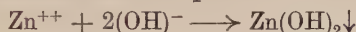
White rust formed on zinc or galvanized surfaces in moist uncontaminated air has usually been found, both in laboratory tests and in practical instances, to consist mainly of a basic zinc carbonate. X-ray analysis has shown this basic carbonate to be usually identical with the compound precipitated from zinc sulphate solution by sodium carbonate, to which the formula $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ has been given. These findings agree with those of Morral.⁶ In some cases the compound formed gives an X-ray diffraction pattern in which the relative intensity of one of the lines is different from usual. This presumably indicates some slight modification in the structure of the basic carbonate.

When white rust attack occurs in air free from carbon dioxide, X-ray analysis of the corrosion product after drying in air for a day or two reveals zinc oxide only. Moreover, white rust samples containing varying proportions of zinc oxide and basic zinc carbonate have been obtained, the proportion of oxide tending to increase when access of air is restricted, e.g. in the interior of coils of wire. In one industrial instance the corrosion product on coils of fine-gauge electroplated wire was found to consist of zinc oxide and basic zinc carbonate in an approximately 2 : 1 ratio. These findings are also similar to those of Morral.^{5, 6}

Zinc hydroxide has not been detected by X-ray analysis of any sample of white rust produced in the present laboratory tests, although in one practical instance α -zinc hydroxide appeared to be present. The failure to detect zinc hydroxide may be either because none is there, or because it occurs in an amorphous form. This latter possibility is not unlikely. For instance, the corrosion product on galvanized sheet immersed in cold supply water, was found on X-ray analysis to be completely amorphous, and no pattern was obtained.

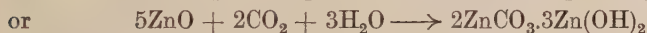
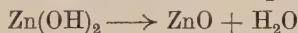
A product containing α -zinc hydroxide, which was prepared by precipitation from zinc sulphate solution with caustic soda in the absence of carbon dioxide, gave an X-ray diffraction pattern different from either zinc oxide or basic zinc carbonate; the material changed partly to zinc oxide on standing in the laboratory at room temperature for a few days. Some forms of zinc hydroxide can therefore dehydrate readily at room temperature.

It is suggested that the primary electrochemical reaction leading to the formation of white rust in the presence of air and water is :



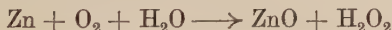
zinc hydroxide being precipitated by interaction of the products from adjacent anodic and cathodic areas.

Secondary reactions which then occur are probably :



Support for the view that the formation of basic carbonate is a secondary reaction is given by the fact that the amount of corrosion occurring in the spray test was the same whether ordinary air or CO_2 -free air was used (Table II), although the corrosion product was basic zinc carbonate in the one case and zinc oxide in the other.

It is considered that this mechanism is more probable than that favoured by Morral,⁵ involving the primary formation of zinc oxide by the reaction :



Even if this reaction did occur, it would appear to be difficult to account for the subsequent formation of basic zinc carbonate, in view of the finding quoted by Morral that " $\text{ZnO.H}_2\text{O}$, once dehydrated cannot take up water to form zinc hydroxide".

Chemical analysis of the corrosion product formed in the distilled-water-spray test (in air containing the normal amount of CO_2), supports the view that the chief substance present is the compound $2\text{ZnCO}_3.3\text{Zn}(\text{OH})_2$, as shown in Table VIII.

The composition of the corrosion product is thus intermediate between that of $2\text{ZnCO}_3.3\text{Zn}(\text{OH})_2$ and that of $\text{ZnCO}_3.2\text{Zn}(\text{OH})_2.\text{H}_2\text{O}$. X-ray analysis showed that both the samples contained small amounts of zinc oxide; this would account for the zinc figure being higher and the combined CO_2 figure being lower than in $2\text{ZnCO}_3.3\text{Zn}(\text{OH})_2$. The basic carbonate present therefore seems likely to be $2\text{ZnCO}_3.3\text{Zn}(\text{OH})_2$.

Observations by Feitknecht and Petermann⁸ during work on the chemistry and morphology of zinc corrosion products are of interest in

TABLE VIII.—Composition of White Rust and of Basic Zinc Carbonates.

	Theoretical Composition of $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$	Theoretical Composition of $\text{ZnCO}_3 \cdot 2\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$	Analysis : Sample 1	Analysis : Sample 2
Zinc, %	59.5	57.4	58.4	58.5
Combined CO_2 , %	16.0	12.9	14.5	} 26.6
Combined water, %	9.8	15.8	...	
Remainder (combined oxygen), %	14.6	14.0	...	(14.9)

connection with the present work. These workers show that six well-defined forms of zinc hydroxide exist, several of which are formed when zinc corrodes in immersed conditions. The stable form is ϵ -zinc hydroxide, and other forms tend to change to this: α -, β -, and amorphous zinc hydroxide are all unstable, and may change either to zinc oxide or to more stable forms of hydroxide. Feitknecht and Petermann found that when zinc corroded in distilled water the chief corrosion products, which were probably formed by transition of the first-formed amorphous zinc hydroxide, were β -zinc hydroxide and zinc oxide.

The presence of zinc oxide in white rust, and the failure to detect zinc hydroxide, is therefore not surprising. The conditions evidently favour the ultimate formation of zinc oxide, or in the presence of carbon dioxide, basic zinc carbonate.

Feitknecht and Petermann confirm that electrochemical action plays an important part in the corrosion of zinc in distilled water. They conclude that the speed of the reaction is largely controlled by the protective action of the corrosion product, which depends on its chemical nature, and on its mode of formation.

During the experiments on corrosion by pools of distilled water, there was a tendency for the most severe attack to occur as a band of localized pitting round the perimeter. Once the oxygen initially present has been used up, the availability of oxygen is greatest round the perimeter, since the diffusion path through the liquid is shortest here. There is, however, no well-defined outer cathodic zone with a central anodic area such as occurs when a pool of sodium chloride solution is placed on steel. This is because of the low conductivity of the distilled water and also because the rate of attack of zinc by distilled water is less than that of steel by chloride solution, and differences of oxygen concentration in the pool are therefore less readily established. Corrosion therefore proceeds very close to the most effective cathodic zones at the perimeter. Some localized attack less intense than that at the perimeter would, however, be expected in the centre of the pools.

The distinction between the inner zone and the outer zone of intense localized attack becomes more noticeable as the size of the pool increases. This electrochemical mechanism explains why a given volume of water as small pools causes more corrosion than the same volume as large pools, the average intensity of attack per unit area being greater with the smaller pools.

Severe corrosion can be produced in moist environments containing substances other than ordinary air, but in these cases the mechanism may be different. Thus, in the presence of sufficient sulphur dioxide, water deposits on the surface, and much attack occurs with the formation of zinc sulphate. In the presence of hydrochloric acid vapour the corrosion product is largely zinc oxychloride. In the presence of vapours of organic acids the rate of attack is also much increased, and zinc salts of fatty acids have been detected in the corrosion products.

On the other hand, when relatively large amounts of ammonia or carbon dioxide are present in the atmosphere the rate of attack is reduced, owing presumably to the production of corrosion products in a more protective form.

IX.—PRACTICAL IMPLICATIONS.

White rusting in practice may be due to one of three causes:

- (1) The action of condensed or entrapped water which remains on the surface for periods of more than a few hours.
- (2) The action of certain acid vapours in moist atmospheres (particularly sulphur dioxide, hydrochloric acid, and organic acids).
- (3) Flux residues on galvanized surfaces.

To avoid white rusting it is necessary to ensure that none of these causes is present, or alternatively to give some protection to the zinc coatings; a simple chromate treatment such as a 10 sec. dip in an acidified 1% sodium dichromate solution has been found to give good protection. It would also be advantageous to quench articles in dilute dichromate solutions immediately after galvanizing; this should give considerable protection against the action of flux residues or condensing water.*

The conditions which will lead to condensation of appreciable amounts of water on zinc surfaces involve (a) a humid atmosphere, and (b) cooling of the metal surface below the temperature of the surrounding air. For instance, if a large mass of metal is stored in an unheated building, the temperature of the metal can fall considerably during the

* In practice it is necessary to rinse articles after chromating to avoid yellow stains. Care must be taken to prevent mechanical damage to the chromate films (particularly before they are dry) and they should not be heated to temperatures above about 70° C., if optimum protection is to be obtained.

night. If, next morning, warm air of high humidity comes into contact with the metal, much condensation will occur. This is observed in practice when on misty or foggy mornings condensation appears on metal stored in buildings partly open to the outside atmosphere. If metal is stored in a room which is not affected by outside humidity changes, there is much less chance of condensation on the metal. If a room containing warm air is cooled by conduction through the walls there is likely to be much more condensation on the walls than on the metal inside the room. In such circumstances it is, however, possible for condensed water to run from the ceiling or the walls on to the stored metal, and so produce white rust.

In the experimental work described it has not been found possible to produce large amounts of white rust inside coils of wire by causing condensation, or by the action of acid vapours including those from insulating tape. Only when bundles of wire were actually dipped in distilled water was white rust produced in the interior. It therefore appears that for severe corrosion to occur in the interior of coils it is necessary for water to penetrate inside. The circumstances in which this may happen in practice may be rather critical, and a number of factors would affect the issue. Possible causes may be :

- (i) Flux or electroplating residues on the wires; (ii) coils so loosely wound that water condensed on the outside easily runs into the interior; (iii) exposure in atmospheres highly contaminated with sulphur dioxide; (iv) coils of wire not properly dried before winding.

Of three practical instances of white rusting which have been investigated in recent years, one was due to rain-water, one was probably due to sulphur dioxide in the atmosphere, and one may have been due to condensation. In view of the small number of practical cases examined, however, it is not possible to say which of the various factors mentioned in this paper are the most important in practice.

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ROLLING AND MECHANICAL PROPERTIES **1270** OF MAGNESIUM ALLOY SHEET CONTAIN- ING 0-9.5% ALUMINIUM.*

By A. E. L. TATE,† A.I.M.

(Communication from The National Physical Laboratory.)

SYNOPSIS.

The results of work carried out on the rolling of cast magnesium alloy ingots into sheet and some mechanical properties of the sheet are described. The alloys contained from 0 to 9.5% aluminium with 0.3% manganese. For the successful rolling of ingots $13 \times 7 \times 1.5$ in. containing more than about 6% aluminium, it was particularly necessary to produce castings free from microporosity. This was achieved by rapid solidification in a smooth-surfaced mould of heavy section.

It was found that, after homogenizing at 400°C ., the ingots containing up to 7% aluminium can be given 75% reduction between 400° – 475°C . at a rolling speed of 180 ft./min. without reheating. The plates obtained are free from defects and rolling can be continued to 95% reduction without an excessive degree of edge-cracking. For ingots containing more than 7% aluminium both the effective rolling temperature and the amount of reduction are substantially reduced. Although materials of higher aluminium content can be reduced to sheet, a tedious procedure is necessary, and as the mechanical properties are not greatly superior to those of alloys containing less aluminium, the 7% alloy is considered to be the practical limit of composition.

Reheated plate and sheet materials containing more than about 6% aluminium do not respond satisfactorily to further rolling at temperatures above about 400°C ., as cracking often develops. The variations in rolling temperature, reduction, and speed are reflected in the mechanical properties.

Hot-rolled sheets containing from 6% to a maximum of 8% aluminium may be cold rolled by a critical amount in the same direction as the previous hot rolling, to improve the proof stress, while retaining a fair measure of ductility. Excessive cold rolling introduces serious directional effects and a marked fall in elongation. Hot-rolled sheet alloys of duplex constitution (the 7–9% aluminium range) do not show any improvement in tensile properties after solution-treatment followed by precipitation-hardening, although the Brinell hardness increases.

The cold-bending qualities of the hot-rolled sheet of the higher-aluminium alloys are good and may be improved by annealing.

The most economical method for producing sheet in the 7% alloy is by rolling at 400° – 475°C . direct from the cast ingot to the finished thickness. Alternatively, where it is desirable to increase the proof stress, the application of a small but somewhat critical amount of cold work is recommended.

Comparative tensile properties of sheet produced by hot rolling alone and of sheet finished by cold rolling are 13–14 against 15 tons/in.² for the 0.1% proof stress; 20–22 against 22–23 tons/in.² for the ultimate tensile stress; and 20–25% against 8–10% for the elongation.

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I.—INTRODUCTION.

DURING recent years much work has been carried out at the National Physical Laboratory with the object of preparing magnesium alloy sheet from cast ingots without extrusion. The chief requirements were that the sheets should be rolled easily and economically, and at the same time have high strength combined with good ductility. Although many complex alloys were investigated in exploratory work, the binary magnesium-aluminium alloys showed themselves to be the most promising. These alloys are already used in industry, though the aluminium content does not normally exceed 5%, except in the case of Elektron AZM, which contains 6% aluminium with 1% zinc.

Experiments were made, therefore, to determine the greatest amount of aluminium that could be added to ingots intended for rolling into sheet, consistent with good fabrication, recovery, and mechanical properties. To this end, the rolling behaviour and properties of alloys containing up to 9% aluminium with 0.3% manganese were studied in detail. In the present paper an account is given of the main features of the earlier work, together with the results of more recent investigations, but not necessarily in chronological order. Detailed accounts of the earlier experiments are given in reports issued by the Aeronautical Research Committee,¹ copies of which have been deposited in the archives of the Institute, with some supplementary information used in preparing this paper.

II—EXPERIMENTAL PROCEDURE.

1. *Materials Used.*

During the course of the work the quality of the basis metal altered. At first electrolytic magnesium of 99.92% purity was used; later, a change was made to ferro-silicon-reduced metal of 99.96% purity. A limited number of comparative tests indicated, however, that the improved quality did not cause noticeable difference in the rolling behaviour, when equally satisfactory ingots were used for rolling.

2. *Melting and Casting.*

The alloys were made in a gas-fired crucible furnace without superheating and the size of the cast ingot used throughout the investigation was $13 \times 7 \times 1\frac{1}{2}$ in., weighing approximately $10\frac{1}{2}$ lb. In casting, the metal was first poured down the edge of the mould, tilted at 45° ; later the mould was raised to the vertical. The pouring rate was standardized by the use of a V groove, $1\frac{1}{2}$ in. wide and $\frac{1}{2}$ in. deep, cut into the edge of the mould; this ensured central feeding and a uniform rate of pouring.

Rapid solidification, which was essential in order to avoid microporosity in the higher-aluminium alloys, was achieved by keeping the metal and mould temperatures as low as was consistent with satisfactory filling of the mould, and by the use of a thick cast-iron mould having a mould-section/casting cross-section ratio of 4 : 1. A ratio of 2 : 1 proved unsatisfactory. The most favourable casting and mould temperatures were 720° and 120° C., respectively.

A mould with an unsuitable surface or mould dressing produced an ingot that cracked in the early stages of rolling. This effect is illustrated in Figs. 1 and 2 (Plate XVIII) in which two 6% aluminium alloy rolled plates are compared, one produced from a slab cast in a mould dressed with a chalk-boric acid mixture and the other from an ingot cast in a smooth mould having no dressing. The procedure finally adopted was to prepare a very smooth surface by coating the mould with a mixture of graphite and oil. Although alloy ingots with less than 6% aluminium normally gave little trouble in rolling, they could be made to crack if they were cast in a mould having rough surfaces. This occurred in spite of the fact that the ingot surfaces were removed to a depth of $\frac{1}{16}$ -in. before rolling. The explanation of this is not clear.

3. *Rolling.*

The size of ingot generally used in the rolling experiments was $7 \times 5 \times 1\frac{1}{2}$ in., cut from the larger cast ingot. This produced a sheet approximately $48 \times 10 \times 0.08$ in. Although these dimensions are small from the commercial point of view, they are considered sufficiently large to indicate the possibility of successful application of the casting and rolling techniques on a larger scale.

4. *Testing.*

The tensile tests were made on test-pieces machined to dimensions required by Air Ministry Specification No. D.T.D. 125 (dated 1933) for hard-rolled magnesium alloy sheet. The tests were made in the Engineering Division of the Laboratory. The proof load was measured by taking a load/extension curve, recording an unloading line from a suitable load, and drawing a line parallel to it to pass through the point of 0.1% permanent extension to intersect the load/extension curve. The point of intersection was deemed to be the 0.1% proof load.

III.—EXPERIMENTAL RESULTS.

1. *Rolling Behaviour of Cast Ingots of Various Aluminium Contents.*

The machined ingots were all heat-treated for 20 hr. at $395^\circ \pm 5^\circ$ C. as a standard procedure before rolling, in order to effect a substantial

degree of homogenization. No special difficulty was experienced in rolling ingots containing less than about 6% aluminium, but it was essential for ingots of higher aluminium content to be free from micro-porosity, as mentioned above. Provided, however, that the ingots were sound and free from segregation, they could be satisfactorily broken down to varying degrees—depending upon the aluminium content—without defects appearing.

In the early stages of the work it was customary to start rolling at a temperature not higher than 400° C. for alloys containing up to 7% aluminium and not above 380° C. for alloys containing more than 7%. It was later found possible, and indeed advantageous, to raise the initial rolling temperature to 450°–475° C. for alloys containing 7% aluminium and to 425° and 400° C. for alloys containing 8 and 9% aluminium, respectively. In these experiments the oxidation of the alloys, and the tendency of the metal to pick up on the rolls,* appeared to set the upper limit to the rolling temperature when the aluminium content was below 7%, and the mechanical failure of the metal when the aluminium content exceeded this amount. The 7% alloy could be rolled satisfactorily from temperatures between 400° and 475° C. and reduced by about 75% without defects. The reduction per pass in the first few passes appeared to be limited only by the capacity of the mill and the ability of the metal to be gripped by the rolls, which were 15 in. in dia. Ingots could be reduced to about 0.08–0.1 in. thick, (i.e. 90% reduction) at 450°–475° C. without reheating and without excessive edge-cracking. For alloys containing 8 and 9% aluminium the limits of reduction from the cast ingot were about 60 and 40% at starting temperatures of 425° and 400° C., respectively. When a point was reached at which deformation effects were not substantially removed by self-annealing in between successive passes, the material failed by the characteristic type of transverse shear cracking shown in Fig. 3 (Plate XIX).

2. Influence of Aluminium Content on Rolling Behaviour of Plates and Sheets.

When intermediate reheating of plates was carried out, it was found that alloys containing more than 6% aluminium exhibited hot cracks on further rolling at 450°–500° C. This was severe in the case of the 8 and 9% alloys, as shown in Fig. 4 (Plate XIX), but much less severe in the 7% alloy (Fig. 5, Plate XIX). If, however, the latter material was given a heavy reduction of the order of 40% in the first pass the defect

* The rolls were not lubricated except when the initial rolling temperature did not exceed 380° C., in which case a mixture of 3 parts of transformer oil with 1 part of paraffin uniformly applied might be employed.

was not always apparent, but this rolling treatment was detrimental to the mechanical properties of the sheet although the finished material had a good appearance. The hot cracks were thought to be due to

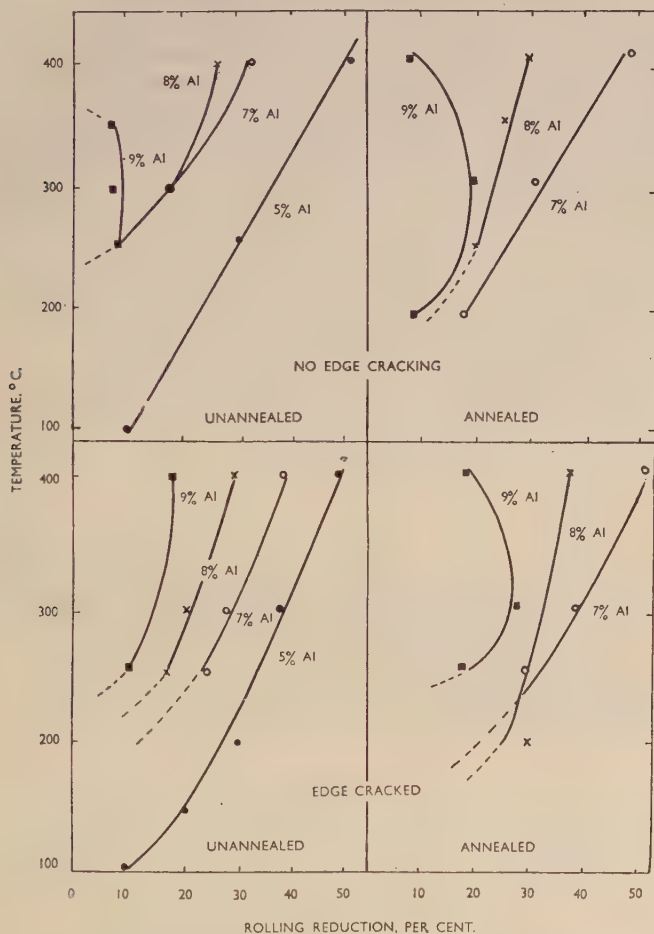


FIG. 18.—Reduction Limits for Magnesium-Aluminium Alloy Hot-Rolled Sheet, 0.09 in. thick, Rolled at 160 ft./min.

excessive grain growth brought about by reheating at high temperatures, but the cause of the defect is not fully understood.

The general effect of the aluminium content on the behaviour of reheated sheets in rolling is illustrated in Fig. 18. A number of 0.09-

in.-thick sheets with aluminium contents between 5 and 9% were prepared, some in the annealed condition (heated for 15 min. at 350° C.) and some hot rolled. They were heated to various temperatures between 100° and 400° C. and given successively larger reductions in a single pass, so as to determine the greatest reduction that could be withstood (*a*) without any cracking, and (*b*) with a tolerable amount of edge cracking. At every temperature the permissible amount of reduction decreased with increasing aluminium content of the alloy. The 5% alloy could withstand appreciable reductions at temperatures below 200° C., but the others could not. With the exception of the 9% alloy all the materials could withstand greater reductions at higher rolling tem-

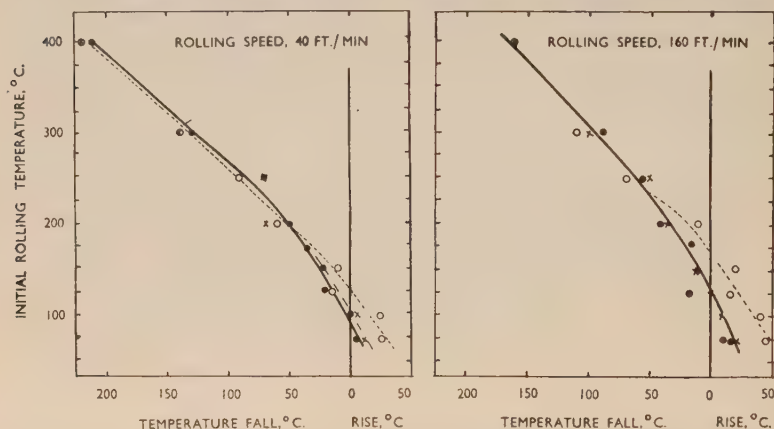


FIG. 19.—Effect of Reduction and Rolling Temperature on the Temperature of Magnesium-5.5% Aluminium Alloy Sheet Rolled at 40 and 160 ft./min.

KEY: ● 10% reduction; × 20% reduction; ○ 30% reduction.

peratures, but the behaviour of this alloy deteriorated when the rolling temperature was above 350° C. All the alloys behaved better in the annealed than in the as-rolled condition. The greater stubbornness of the high-aluminium alloys is probably attributable to the hard β constituent, which was present as scattered particles in both the as-rolled and the annealed alloys when the aluminium content exceeded 7% (Figs. 6 and 7, Plate XX).

3. Influence of Rolling Conditions on Tensile Properties.

The experiments described were made with a peripheral rolling speed of 160 ft./min., using rolls heated to about 100° C. The behaviour was sensitive to the initial condition of the metal and to the precise conditions of rolling. The temperature of the metal (as measured with a

clip pyrometer) generally fell during the pass if the initial rolling temperature was above about 150° C., but increased if it was lower. The temperature change depended on the degree of reduction and the speed of rolling, and the final temperature influenced the final properties of the sheet.

In Fig. 19 the temperature changes in a 5.5% aluminium alloy are illustrated, and Fig. 20 shows how the rolling variables were related to the tensile properties of the sheet. As might be expected, a large reduction and a high speed of rolling increased the finishing temperature of the sheet, the effect being particularly noticeable at the lower rolling

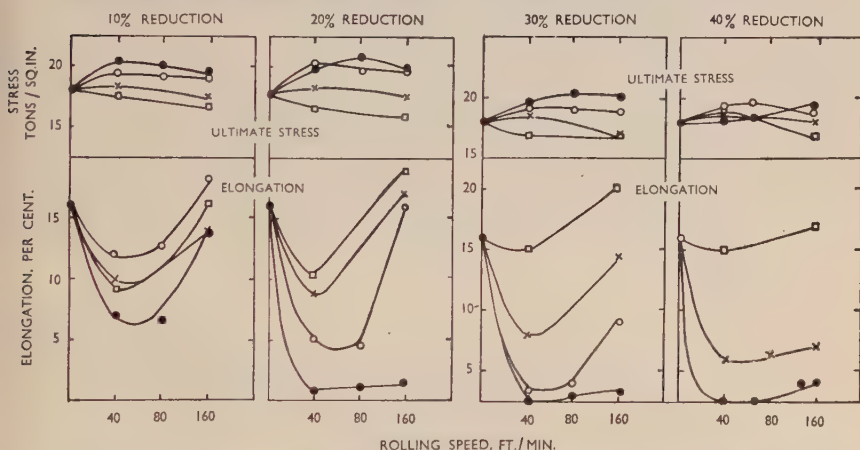


FIG. 20.—Effect of Rolling Conditions on the Tensile Properties of Magnesium-5.5% Aluminium Alloy Sheet.

KEY: ● Rolled at 150° C.; ○ Rolled at 200° C.; × Rolled at 300° C.; □ Rolled at 400° C.

temperatures. The alloys were strongest, and least ductile, when the rolling temperature was low, the rolling speed low, and the degree of reduction high. Fast rolling made it possible to improve the elongation without any great sacrifice of tensile strength, and by suitable choice of conditions a very useful combination of properties could be secured. Rapid deformation helped to prevent the temperature of the sheet falling below the limit at which recovery and recrystallization could take place, and it was found that greater reductions could be withstood at low temperature than were possible when low rolling speeds were employed. Similar general conclusions applied to alloys with 7 and 8% aluminium, but it did not appear possible to improve the elongation of the 9% alloy by the use of high rolling speeds.

The importance of the chilling effect of the rolls and the compensating influence of the heat generated by the work done on the metal is illustrated by the following experiment. Three sets of sheet of 5.5% aluminium alloy, about 0.10 in. thick, were prepared in such a way as to have a fully recrystallized fine-grained structure, with a tensile strength of 17 tons/in.² and an elongation of 22%. Samples from the first set were raised to a series of temperatures between 75° and 300° C. and given a single reduction of about 25% with rolls at 100° C. and using a slow rolling speed of 20 ft./min. The second set was treated similarly except that the rolling speed was 160 ft./min., while the third set was

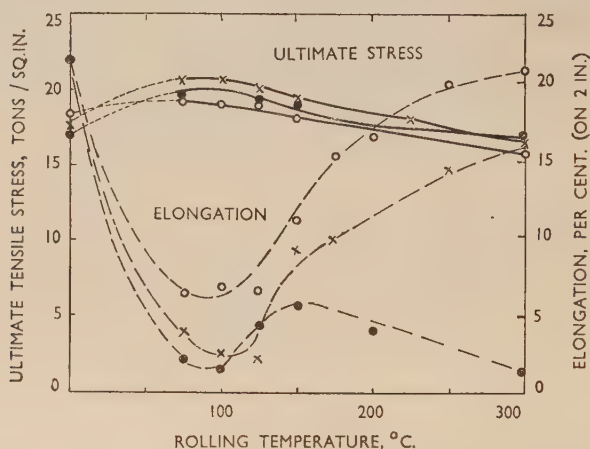


FIG. 21.—Relative Effect of Rolling Temperature and Roll Temperature on the Tensile Properties of Magnesium-5.5% Aluminium Alloy Sheet.

KEY: ● 23 25% reduction in slow mill at 20 ft./min.; × 25% reduction in large mill at 160 ft./min., rolls at 100° C.; ○ 21-30% reduction in slow mill at 20 ft./min., rolls and metal at same temperature.

rolled at 20 ft./min. in a specially designed equipment in which the surface temperature of the rolls could be adjusted to that of the sheet. The sheet was held at constant temperature in an oil bath up to the moment at which it was delivered to the mouth of the rolls.

The tensile properties of the resulting sheets are shown in Fig. 21. The slowly-rolled sheets whose temperature had been prevented from falling by the use of hot rolls proved throughout the weakest and most ductile of the series, but were closely approached by the quickly-rolled sheets, which, however, were somewhat harder and less ductile. The sheets that had been rolled slowly between cool rolls were intermediate in strength, but when the initial rolling temperature was above 150° C. they were considerably poorer in ductility. Fig. 21 also illustrates the

general effect of the rolling temperature upon the tensile properties of the sheet.

Rolling under ordinary conditions at temperatures above 300° C. produced material having a tensile strength of 15–17 tons/in.² with about 20% elongation, and as the rolling temperature decreased to 100° C. the strength increased moderately to about 20 tons/in.², while the elongation decreased very sharply to about 5%. When the reduction was around 25%, 150°–200° C. was the lowest temperature that could be used without producing an unacceptably brittle sheet, and when the reduction was larger, the rolling temperature had to be increased. These changes were reflected in the microstructure of the sheet. High ductility was associated with a reasonably uniform aggregate of fine equi-axed grains (Fig. 8, Plate XX). Inferior ductility was first indicated by the appearance of bands of coarse and fine grains (Fig. 9, Plate XX), while very low ductility was accompanied by strain bands and a clearly distorted grain structure (Fig. 10, Plate XX).

4. Mechanical Properties of Hot-Rolled Sheets.

The results of tensile tests on a series of hot-rolled sheets with aluminium contents up to 9.5% are given in Table I. The sheets were

TABLE I.—*Effect of Aluminium Content and Rolling Temperature on Tensile Properties of Magnesium Alloy Sheets.*

Aluminium, %	Rolling Temperature, ° C.	Tensile Test Results					
		Longitudinal			Transverse		
		0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.	0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.
1.4	400	10.0	15.8	13	11.3	16.3	19
5.0		11.0	18.3	13	13.2	18.8	19
6.0		12.0	19.0	16	13.2	19.1	11
7.0		13.1	20.8	21	14.7	20.8	22
9.5		14.3	22.3	12	14.6	21.8	10
8.5	350	12.7	21.9	12	15.4	22.8	15
9.5		14.5	22.7	15	15.2	22.9	16
1.4	300	10.6	16.2	15	12.3	16.6	20
5.0		11.6	18.3	19	13.2	18.7	25
6.0		12.3	19.3	19	13.8	19.8	19
7.0		11.3	20.4	23	14.7	20.6	19
9.5		16.6	24.0	3	16.5	24.3	9
1.4	250	10.7	15.8	...	12.6	16.8	14
5.0		13.3	19.3	16	15.1	19.6	18
7.0		15.1	21.6	14	16.4	22.8	11

0.065 in. thick, and had been rolled from 0.10 in. by a single pass at 160 ft./min., through rolls heated to 100° C.

When rolled at 400° or 300° C., the sheets all showed progressively increasing proof stress, ultimate stress, and elongation values as the aluminium content increased from 1.4 to 7.0%. Above 7% aluminium, the proof stress and ultimate stress continued to rise, but the elongation fell appreciably in sheets rolled at 400° C., and very seriously in sheets rolled at 300° C.; in sheets rolled at 250° C. the fall in elongation was perceptible when the alloys contained more than 5.5% aluminium. Alloys containing more than 7% could not be rolled at 250° C. The best general properties were obtained with the 7% alloy, in which an ultimate stress of 20 tons/in.², combined with a 0.1% proof stress of 12–14 tons/in.² and an elongation of 20%, could be secured.

Directionality was not marked. The transverse direction gave on the whole a slightly higher proof stress and elongation. In this connection it should be noted that the sheets had been turned through 90° after every pass while being reduced from 1.4 in. to 0.3 in. thick, and thenceforward had been rolled in one direction only.

Cold-bend tests made with Glaysher's machine² confirmed the general conclusions obtained from the tensile tests. Table II gives the results of tests on a series of alloys of increasing aluminium content, in which sheet approximately 0.10 in. thick was produced by giving final reductions of 30% at initial rolling temperatures varying from 400° to 200° C., the result of the bend test is recorded in columns 6 and 7 of the table in terms of the smallest radius over which the sheet could be bent through 90° without cracking, this radius being expressed as a multiple of the sheet thickness. The bending properties generally improved with increase of aluminium content; rolling at 400° or 300° C. produced relatively ductile material free from directionality, while rolling at lower temperatures introduced directionality and resulted in a general deterioration of the properties. The bending properties resulting from rolling at low temperatures were worse in the longitudinal direction than in the transverse direction. These effects were more serious in alloys with aluminium contents above 5%, with the result that the bending properties of high-aluminium alloys rolled at the lower temperatures were inferior to those of similarly rolled alloys of intermediate aluminium content. Similar general results were obtained in sheet rolled to 0.07 in. or 0.04 in. thick, and it was noticeable that directionality was most commonly produced in the alloys of lowest aluminium content. Sheet about 0.1 in. thick containing 7% aluminium and finally rolled by giving 20–25% reduction in 1–2 passes at 400°–380° C. had proof stress, ultimate stress, and elongation values of 12–15

Magnesium Alloy Sheet Containing Aluminium 81

TABLE II.—*The Cold-Bending Properties of Magnesium-Aluminium Alloy Sheets of Various Thicknesses Rolled at Various Temperatures.*

Aluminium, %	Rolling Temperature, ° C.		Thickness, in.	Reduction, % on last pass	T Value *	
	Starting	Finishing			Longitudinal	Transverse
A. Sheet Approximately 0.10 in. Thick						
0.0	400	250	0.085	29	7	7
1.41		265	0.090	32	6	5
3.84		280	0.100	29	6	5
6.73		220	0.085	27	4	4
7.96		280	0.100	30	4	4
0.0	300	210	0.085	30	6	6
1.41		260	0.090	...	5	5
3.84		250	0.097	30	4	4
6.73	
7.96		240	0.106	26	4	4
0.0	250	200	0.085	34	10	5
1.41		200	0.098	29	6	4
3.84		200	0.095	33	6	4
7.96		200	0.097	25	8	6
0.0		200	180	0.086	31	10
1.41	190		0.098	32	8	4
3.84	190		0.095	28	4	4
6.73
7.96	190		0.097	25	8	7
B. Sheet Approximately 0.07 in. Thick						
0.0	400	250	0.064	22	7	5
1.41		260	0.063	32	7	5
3.84		270	0.067	32	7	5
6.73		260	0.064	26	5	5
7.96		260	0.064	35	5	5
0.0	300	230	0.068	17	6	5
1.41	
3.84	
6.73	
7.96		240	0.075	25	7	6
C. Sheet Approximately 0.04 in. Thick						
0.0	400	220	0.031	50	9	5
1.41		220	0.035	44	7	5
3.84		230	0.044	35	5	5
6.73		230	0.042	30	5	5
7.96		230	0.043	35	5	5
0.0	300	180	0.035	35	8	6
1.41		180	0.040	36	7	7
3.84	
6.73	
7.96		190	0.055	29	9	8

* $T = \frac{d}{2t}$, where d = dia. of former, t = thickness of sheet.

TABLE III.—*The Effect of Cold Rolling on Tensile Properties of Hot-Rolled Magnesium-Aluminium Alloy Sheets.*

Alu- minium, %	Direction of Test	Sheet Rolled at 400° C. (Finishing temp. about 270° C.)										Sheet Rolled at 300° C. (Finishing temp. about 220° C.)							
		As Hot Rolled			5% Cold Work			10% Cold Work			15% Cold Work			As Hot Rolled			5% Cold Work		
		0.1% Proof Stress, tons/ in. ²	U.T.S., tons/ in. ²	Elong- ation, % on 2 in.	0.1% Proof Stress, tons/ in. ²	U.T.S., tons/ in. ²	Elong- ation, % on 2 in.	0.1% Proof Stress, tons/ in. ²	U.T.S., tons/ in. ²	Elong- ation, % on 2 in.	0.1% Proof Stress, tons/ in. ²	U.T.S., tons/ in. ²	Elong- ation, % on 2 in.	0.1% Proof Stress, tons/ in. ²	U.T.S., tons/ in. ²	Elong- ation, % on 2 in.	0.1% Proof Stress, tons/ in. ²	U.T.S., tons/ in. ²	Elong- ation, % on 2 in.
0.00	Long. Trans.	...	10.9 15.1	5.2 5.7	...	12.4 15.85	1.7 5.7	13.10 15.95	1.3 7.2	...	11.4 16.5	0.8 8.0	...	11.0 15.3	3.5 8.2	...	11.7 15.75	...	0.5 6.7
1.85	Long. Trans.	...	16.25 16.95	17.7 22.7	...	17.3 19.1	4.5 10.0	17.35 19.8	3.0 10.7	...	5.6 20.7	0.0 4.2	...	15.95 17.0	10.7 17.0	...	17.4	3.0 ...
3.75	Long. Trans.	...	17.15 17.4	22.7 27.0	...	18.7 19.1	5.0 13.0	19.5 20.85	3.5 12.0	...	12.6 21.95	0.5 4.0	...	17.2 18.15	17.5 24.0	11.6 13.9	19.05 19.7	...	9.0 12.5
4.99	Long. Trans.	...	17.2 17.85	21.5 20.0	...	17.4 19.95	4.0 14.0	19.5 20.5	5.7 8.0	...	14.7 22.9	17.6 17.55	19.5
5.66 *	Long. Trans.	11.0 13.2	18.4 18.9	22.7 25.7	13.9 13.8	20.55 21.3	14.5 16.2	20.8 22.45	2.5 13.0	16.9 16.8	20.8 22.5	5.2 14.5	...	18.25 19.6	12.2 25.2	13.2 13.7
6.73 †	Long. Trans.	13.1 14.7	19.65 19.85	23.7 23.0	16.4 15.2	20.8 21.0	14.3 20.0	22.25 23.9	9.2 9.0	17.5 17.4	22.45 22.25	9.0 14.7	...	20.2 20.15	24.0 19.0
8.02 †	Long. Trans.	12.3 ...	20.05 21.15	21.7 21.0	13.8 12.7	20.05 21.8	9.5 21.0	22.2 23.9	7.5 12.0	17.6 17.0	23.6 25.0	6.5 10.0	...	20.05 20.35	18.0 12.0	14.9 ...	21.6 22.35	...	9.0 9.5
8.45	Long. Trans.	15.8 14.7	21.5 24.1	5.0 13.0	16.4 16.5	23.7 25.5	3.0 7.0

* Proof-stress determinations made on alloy containing 5.82% Al.

† Proof-stress determinations made on alloy containing 6.82% Al.

‡ Proof-stress determinations made on alloy containing 7.96% Al.

tons/in.², 19–22 tons/in.², and 15–12%, respectively. Material which had been rolled from the cast ingot without reheating at starting temperatures of 450° and 475° C., gave proof and ultimate stress values of 13–14 and 21–22 tons/in.², respectively, with more than 15% elongation. In sheet which was reduced from 0.25 in. thick to about 0.09 in. thick in 3 passes at starting temperatures of 400° and 450° C., however, the ultimate stress was reduced to 14–18 tons/in.² and the proof stress to 9–10 tons/in.², with elongation values varying between 2 and 15%. The reason for this was not studied, but it is evidently necessary to avoid such a rolling procedure. The cold-bending properties of this material varied considerably and were related to the microstructure of the sheet, as illustrated in Figs. 11, 12, and 13 (Plates XX and XXI). The fully-recrystallized material gives a bending value of 4–5 *T* compared with 10 *T* for sheet in which there is less evidence of recrystallization.

5. The Cold Rolling of Hot-Rolled Sheet.

Sheet that had been hot rolled at 250° C. or below was too hard to be cold rolled satisfactorily, but sheet which had been hot rolled and given 20–25% reduction in the final rolling at 300° C. (finishing temperature 220° C.) and at 400° C. (finishing temperature 270° C.) could be given 5 and 15% cold reduction, respectively. Great care was necessary when cross rolling was attempted. Unless very nearly equal amounts of deformation were given successively in each direction the material collapsed by transverse cracking. Table III shows the results of tensile tests on cold-rolled sheet. Cold rolling raised the proof stress and ultimate stress, but its most striking effect was a very sharp reduction of the elongation in the longitudinal direction. Directionality was very marked in cold-rolled sheets of low aluminium content. Sheets with aluminium contents between 5 and 8% were on the whole less severely affected than others, and in this range of composition it was possible to produce material with proof stress 15–17 tons/in.², ultimate stress 21–24 tons/in.², and elongation values of 6–14 and 10–20% in the longitudinal and transverse direction, respectively. By cold rolling equal amounts alternately in both directions, material with uniform properties, but with comparatively low elongation, could be produced. An attempt was made to improve the ductility of cold-rolled sheet by prolonged annealing at 125° C., in the hope of removing some internal stress without loss of strength. A slight improvement was obtained, but it was neither great enough nor consistent enough to be useful. Sheet containing 7% aluminium which had been rolled from the cast ingot without reheating had a small capacity for cold work, not ex-

TABLE IV.—*Effect of Annealing Temperature and Time of Annealing on Mechanical Properties of Hot-Rolled Magnesium-Aluminium Alloy Sheets Containing 5.5-9% Aluminium.*

Alu- minium, %	Direction of Test	As Rolled			Annealed at 200° C. for 15 min.			Annealed at 200° C. for 30 min.			Annealed at 250° C. for 15 min.			Annealed at 250° C. for 30 min.			Annealed at 300° C. for 15 min.		
		0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elonga- tion, % on 2 in.
5.5	Long. Trans.	11.9 ...	18.3 18.6	18.0 13.5	18.0 ...	15.0	18.0 18.55	13.5 13.0	...	18.0 ...	16.5	18.1 18.3	16.0 13.5	...	17.9 ...	13.5
7.3	Long. Trans.	11.95 ...	19.5 ...	11.0 ...	19.3 ...	9.0	18.2 19.45	7.7 8.5	...	19.5 ...	10.5	19.3 19.25	9.75 8.5	...	18.55 ...	8.0
8.1	Long Trans.	12.3 13.6	19.6 19.8	13.0 17.0	19.2 ...	10.0 ...	12.3 13.6	19.75 19.9	16.0 16.0	...	18.8 ...	10.0	18.6 19.4	8.75 10.0	...	18.6 ...	10.0
8.8	Long. Trans.	13.2 14.8	20.0 20.7	8.0 10.0	19.8 ...	9.0	19.0 20.2	8.0 10.0	12.5 14.15	20.6 19.7	15.5 10.5	...	19.5 19.8	9.5 8.0	...	19.25 ...	8.5

Alu- minium, %	Direction of Test	Annealed at 300° C. for 30 min.			Annealed at 350° C. for 15 min.			Annealed at 350° C. for 30 min.			Annealed at 400° C. for 5 min.			Annealed at 400° C. for 10 min.			Annealed at 400° C. for 20 min.		
		U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.
5.5	Long. Trans.	17.9 18.25	15.75 10.0	...	17.7 ...	13.0	17.8 17.9	14.5 11.0	17.5 ...	14.0	17.6 18.0	13.0 13.5	...	17.6 18.0	15.5 11.7	...	17.6 18.0
7.3	Long. Trans.	18.55 19.15	11.0 8.5	...	17.7 ...	9.5 ...	10.8 ...	18.8 17.8	15.0 9.0	17.9 18.1	11.5 9.5	...	17.6 17.9	11.0 8.7	...	17.9 17.9	10.5 9.0	...	17.9 17.9
8.1	Long. Trans.	18.9 19.4	13.5 12.0	...	17.1 ...	8.5	18.0 18.7	12.0 14.0	17.4 18.5	11.0 12.5	...	18.1 ...	12.0 ...	10.5 11.6	18.6 19.0	16.0 15.0	...	18.6 19.0
8.8	Long. Trans.	19.7 20.0	12.5 10.5	...	18.3 ...	10.5	18.3 18.4	11.5 8.0	17.4 18.9	8.0 10.5	...	18.1 ...	9.5 ...	10.0 11.6	18.0 19.1	11.0 11.7	...	18.0 19.1

ceeding 5%. This is unexpected in view of its elongation, which was of the order of 18–25%. The elongation was reduced to 15–20% by the small amount of cold rolling without affecting materially the proof and ultimate stresses, which were 14 and 22 tons/in.², respectively.

6. Effect of Annealing Hot-Rolled Sheet.

It has already been stated that excessive grain growth in annealed hot-rolled sheet was detrimental to the rolling behaviour. The precise behaviour naturally depended on the conditions of hot rolling, and the following remarks refer to sheet that had been finished with a reduction of 20%, given under conditions which ensured a finishing temperature between 250° and 350° C.

In alloys containing less than 7% aluminium grain growth of the α solid solution was the main change brought about by annealing. It was not marked at 300° C., but perceptible at 350° C. and rapid at 400° C. These alloys were fully softened by annealing for 15 min. at 350° C., and there was no point in annealing at higher temperatures or for longer times. In alloys with 7% aluminium and more, solution of the β constituent was an additional factor. It took place in 10–15 min. at 390° C., but was not complete in an equal time at 350° C. (Figs. 14 and 15, Plate XXI). The β constituent was retained in solution by air-cooling or water-quenching. Provided no excess grain growth occurred, the solution of the β constituent resulted in an appreciable decrease of strength and increase of elongation. The bending properties of alloys low in aluminium tended to suffer as a result of annealing, but the high-aluminium alloys resisted this deterioration, probably because excessive

TABLE V.—*Effect of Time of Annealing at 350° C. on Cold-Bending Properties of Magnesium-Aluminium Alloy Sheets.*

Aluminium, %	T Value.							
	As Rolled		Annealed for 15 min. at 350° C.		Annealed for 30 min. at 350° C.		Annealed for 60 min. at 350° C.	
	Long.	Trans.	Long.	Trans.	Long.	Trans.	Long.	Trans.
...	7	5	7	6	8	6	8	8
0.93	7	5	6	6	7	5	7	6
4.99	5	5	5	4	4	4	6	5
6.73	3	3	5	3	3	3	3	3
8.02	4	4	3	4	3	3	4	3

grain growth was retarded so long as undissolved β constituent was present. The results of tensile tests (Table IV) and bend tests (Table V) illustrate these points.

TABLE VI.—*Tensile Properties of Cold-Rolled Magnesium-Aluminium Alloy Sheet.*

Condition of Material	Rolling Direction	Tolerable Limit of Reduction, %	Tensile Properties *							Cold Bend T' Value
			Before Cold Rolling				After Cold Rolling			
			Direction of Test	0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.	0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.	
(a) Annealed at 350° C.	Longitudinal (original rolling direction)	9	Long. Trans.	11.6 12.4	19.3 19.0	19 18	14.2 15.8	20.3 22.6	6 10	12 10
	Longitudinal and transverse in equal amounts	5	Long. Trans.	11.6 12.4	19.3 19.0	19 18	15.4 15.5	21.2 21.0	11 12	9 8
(b) Solution-treated at 395° C.	Longitudinal (original rolling direction)	5	Long. Trans.	11.6 12.7	19.4 19.5	16 15	14.2 13.9	20.1 21.0	13 14	8 8
	Longitudinal and transverse in equal amounts	10	Long. Trans.	11.6 12.7	19.4 19.5	16 15	15.8 16.9	21.6 21.8	9 10

* Mean of duplicate tests.

7. Cold Rolling of Annealed Sheet.

Sheets that had been suitably annealed could be cold rolled in much the same way as hot-rolled sheets. They withstood a somewhat greater amount of deformation without cracking, and in favourable cases as much as 25% reduction of thickness could be given before the sheet could be said to have failed completely. In a particular series of tests, a 7% aluminium alloy solution-treated at 390° C. so as to take the β constituent into solution (Fig. 15, Plate XXI), showed a slightly greater capacity for cold work than similar sheet annealed at 350° C. and containing unabsorbed β constituent (Fig. 14, Plate XXI).

The mechanical properties of annealed sheets when cold worked were similar to those of hot-rolled sheets given the same degree of cold

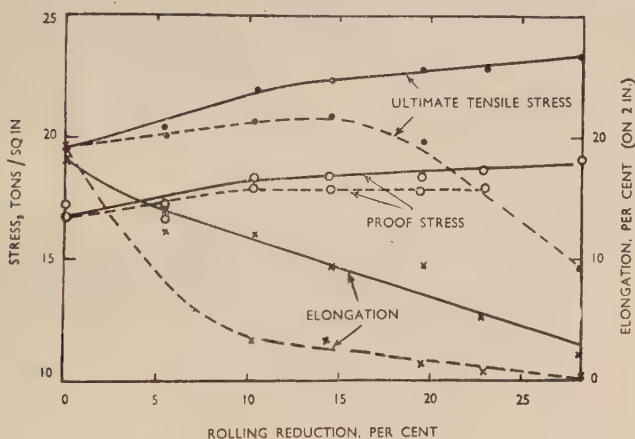


FIG. 22.—Effect of the Degree of Reduction by Cold Rolling on the Tensile Properties of Magnesium-7% Aluminium Alloy Annealed Hot-Rolled Sheet.

----- Longitudinal tests.

————— Transverse tests.

reduction. Table VI shows typical properties obtained in a 7% alloy cold rolled after being heat-treated (a) at 350° C. and (b) at 395° C. A small amount of cold rolling of this alloy gave a very useful increase of proof stress from 11 to 15 tons/in.² at the expense of a fall of elongation to about 10%, but it was not considered desirable to apply more than 5%, or at the most, 10% reduction, on account of the serious fall of elongation and ultimate stress that occurred when large reductions were used. Fig. 22 shows the changes in tensile properties as the 7% alloy solution-treated at 395° C. was progressively cold rolled.

8. *Effect of Solution-Treatment and Precipitation-Hardening.*

Since in alloys containing more than 7% aluminium, the β constituent is taken into solution at high temperatures and precipitated at low, the possibility of improvement by precipitation-hardening exists. Experiments were made on three alloys, containing respectively 7.1, 8.3, and 9.0% aluminium in the form of hot-rolled 0.1-in.-thick sheets. Preliminary trials showed that the β constituent was quickly taken into solution at 380° C. in the 7.1% alloy and at 390° C. in the other two alloys. Consequently, all the samples were initially quenched in water after being heated for 15 min. at 390° C.

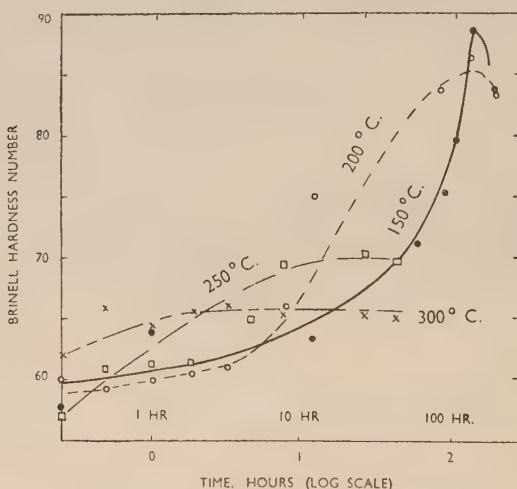


FIG. 23.—Effect of Precipitation Treatments at 150°, 200°, 250°, and 300° C. on Brinell Hardness of Solution-Treated Magnesium-8% Aluminium Alloy Sheet.

Hardening was found to occur on reheating in the range 150°–300° C. The greatest effect was an increase in hardness from about 60 to about 90 Brinell at 150°–175° C. The behaviour of the 8.3% aluminium alloy is illustrated in Fig. 23. Hardening began after 10 hr. at 150° C. and a maximum was reached after about 100 hr. At 175° C. hardening began after 2 hr., and reached a maximum in 80 hr. At higher reheating temperatures the maximum hardness fell progressively. The microstructures after ageing at different temperatures are shown in Figs. 16 and 17 (Plate XXI). The precipitation was discontinuous at 150° C., but not obviously so at higher temperatures. The behaviour of the other alloys was similar, except that the 9% alloy

was somewhat harder throughout, and the 7.1% alloy was softer, and over-aged more readily.

The tensile properties resulting from the ageing treatments which produced maximum hardness are given in Table VII and are unpromising. The hardening was not accompanied by any important increase of tensile strength or proof stress, but there was a serious loss of elongation, and the properties of the solution-treated and aged sheets were on the whole appreciably worse than the best properties of hot-rolled sheets.

TABLE VII.—*Effect of Precipitation-Treatments on the Tensile Properties and Brinell Hardness of Magnesium-Aluminium Alloy Sheets.*

Aluminium, %	Precipitation Treatment	Direction of Test	Mechanical Properties *			
			0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.	Brinell Hardness (2/20/30)
7.0	150° C. for 170 hr.	Long.	11.9	19.9	12.5	67
		Trans.	...	20.4	14.5	...
8.3	150° C. for 100 hr.	Long.	13.6	21.6	7.0	94
		Trans.	...	21.9	6.0	...
9.0	150° C. for 100 hr.	Long.	...	23.4	4.0	92
		Trans.
7.0	} 200° C. for 100 hr.	Long. {	10.9	17.7	6.0	72
8.3			12.0	19.3	5.0	82
9.0			12.6	20.7	5.0	86
7.1	} 250° C. for 8 hr.	Long. {	10.6	18.3	8.5	57
8.3			11.3	17.9	4.0	70
8.3	300° C. for 8 hr.	Long.	11.3	17.7	5.5	67

* Means of duplicate or triplicate tests.

9. Properties of 7% Aluminium Alloy Sheet.

During the course of the experimental work, a large number of tensile tests were made, and it has been thought useful to include a summary of the range of properties secured in sheet containing approximately 7% aluminium. The figures have special reference to sheet about 0.1 in. thick, which is the thickness that it has generally been most convenient to produce.

There seem to be three principal ways of producing such sheet. The first is to roll throughout at temperatures between 400° and 475° C. with heavy pinches and a high speed of rolling, with the object of coming down to the desired thickness without reheating, and finishing at a

temperature of 200°–250° C. to give a fine-grained, moderately soft sheet, free from directional properties. This is the most economical method. It has been found possible in the laboratory to reduce a 1½-in.-thick casting to a 0.08-in.-thick sheet in one operation without excessive edge-cracking. The greatest rolling speeds and reductions attainable with the available mill have been used, and it is, of course, not possible to say how much further in this direction it would be practicable to go. The properties of sheet made in this way are given in Fig. 24. A large proportion of such material has a tensile strength of 21 tons/in.² with a proof stress of 13–14 tons/in.² and an elongation greater than 15%,

but there is a proportion of it in which both the strength and elongation are lower than this, suggesting that occasionally the material has been weakened by over-rolling at too low a temperature. The bending properties of sheet made in this way are also somewhat irregular. Some samples are equal to the best described in Table II, having a minimum radius for satisfactory bending of 3–4 *T*, but others have a minimum radius no better than 8–9 *T*. The average behaviour is about midway between these limits. These data refer to sheet that has been rolled between rolls heated to 100° C.

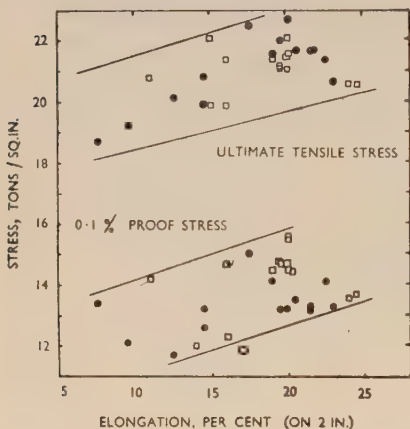


FIG. 24.—Tensile Properties of Magnesium–7% Aluminium Alloy Sheet Rolled from 1.4 in. at 400°–475° C. to 0.1 in. Thick without Reheating.

● Longitudinal tests. □ Transverse tests.

The second method is to reheat to 360°–400° C. at a thickness 25–30% above the finished thickness, and give a single final pass under conditions chosen for the best combination of strength and ductility. Fig. 25 shows the range of properties to be expected. The direction transverse to the direction of the final rolling is slightly the stronger and slightly the more ductile, but there is little difference, and the following tensile-test figures represent a range within which sheets produced in this way will fall :

Ultimate stress : 19–22 tons/in.²
 0.1% Proof stress : 12–15 tons/in.²
 Elongation : 10–25%

The bending properties are usually good, the minimum radius for satis-

factory bending being generally 3–5 *T*. The higher strengths are usually associated with the lower elongations, but the correlation is not close, and proof stresses above 15 tons/in.² are frequently associated with elongations greater than 20%.

Finally, if a high proof stress is required at a sacrifice of ductility

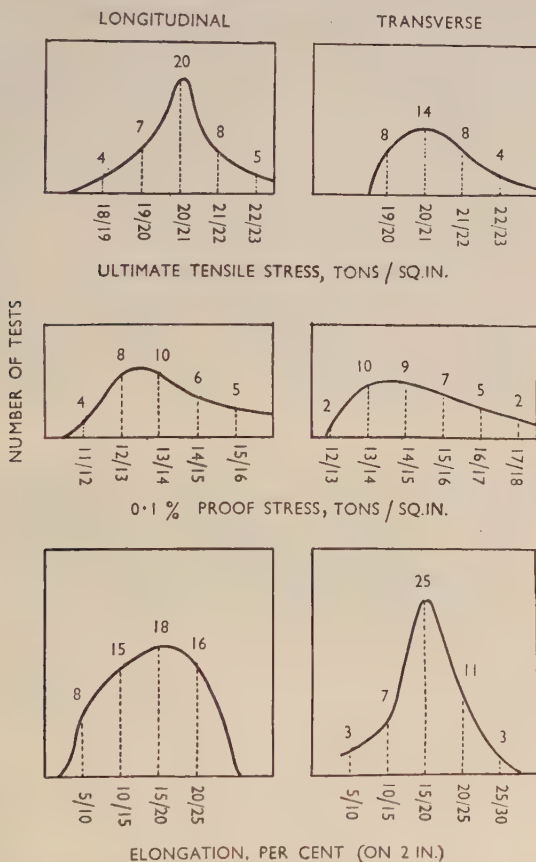


FIG. 25.—Tensile Properties of Magnesium-7% Aluminium Alloy Sheet Hot-Rolled with Final Reduction of 20–30% at Starting Temperature of 360°–400° C.

and bending properties, a short “solution-treatment” at 400° C., followed by a cold reduction of 5–10% can be used to give the range of properties illustrated in Fig. 26. The 0.1% proof stress can be raised to 15 tons/in.² minimum, but the elongation may fall to as little as 10%, and the behaviour in the bend test is not good. The tensile strength

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of sheet in the hot-rolled, recrystallized state can also be increased by cold rolling, but the cold rolling of solution-treated material is considered to be a safer method. This method may be preferable since flatter sheets can be produced than by hot rolling, thus reducing the need for roller-levelling. Roller-levelling of magnesium alloy sheet materials

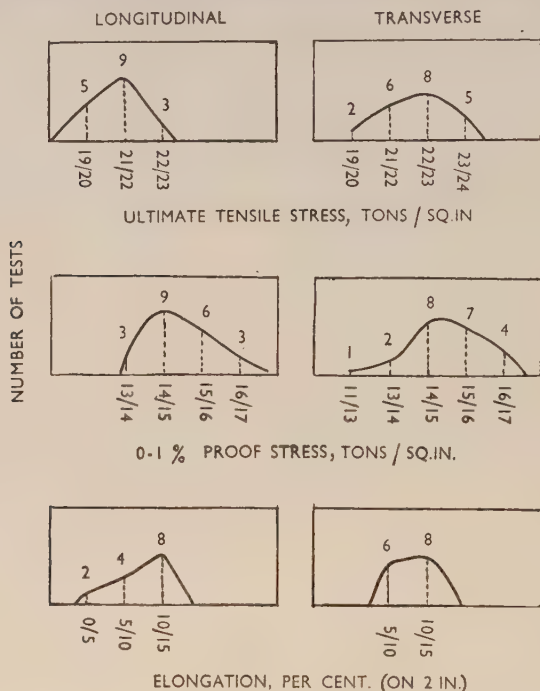


FIG. 26.—Tensile Properties of Magnesium-7% Aluminium Alloy Sheet after Solution-Treatment at 400° C. and 5-10% Reduction by Cold Rolling.

is known to be detrimental to the tensile properties and some work on roller-levelling effects is in progress at the National Physical Laboratory.

ACKNOWLEDGEMENTS.

The work described above was carried out as part of the research programme of the National Physical Laboratory, and much of it was conducted under the direction of Dr. J. L. Haughton. The paper is published by permission of the Director of the Laboratory.

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2. G. H. Glaysher, *J. Inst. Metals*, 1942, **68**, 383.



FIG. 1.—Rolled slab cast in mould having smooth surfaces.



FIG. 2.—Rolled slab cast in a dressed mould having rough surfaces.

FIGS. 1 and 2.—Effect of Surface Condition of Mould on Rolling Behaviour of Cast Magnesium-6% Aluminium Alloy Ingots, 1.5 in. thick.

[To face p. 92.

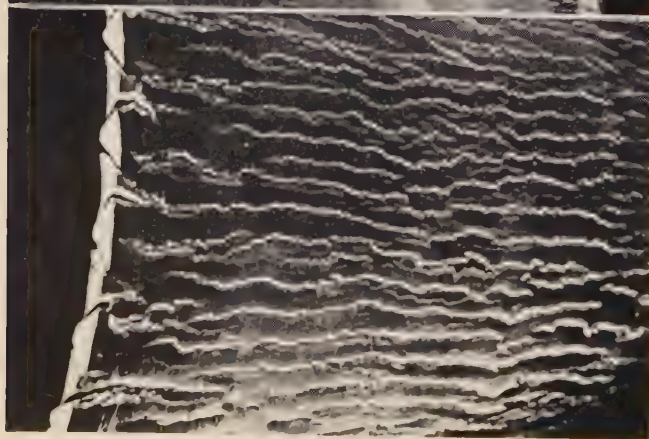


FIG. 3.—Transverse shear cracking in rolled plate.

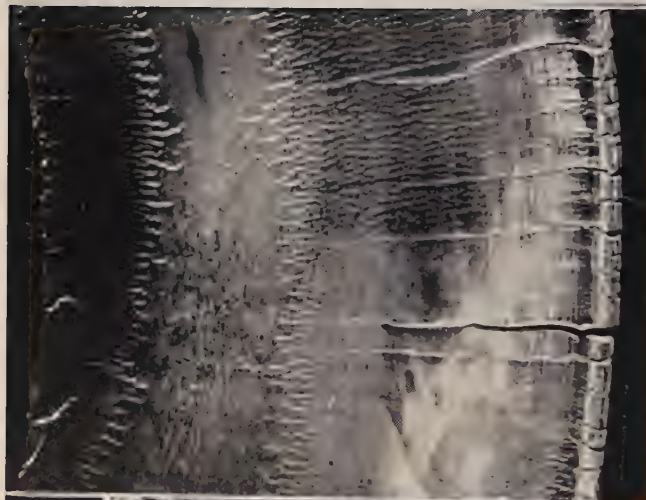


FIG. 4.—Transverse "hot cracking" in reheated magnesium-8% aluminum alloy plate rolled at 450° C.

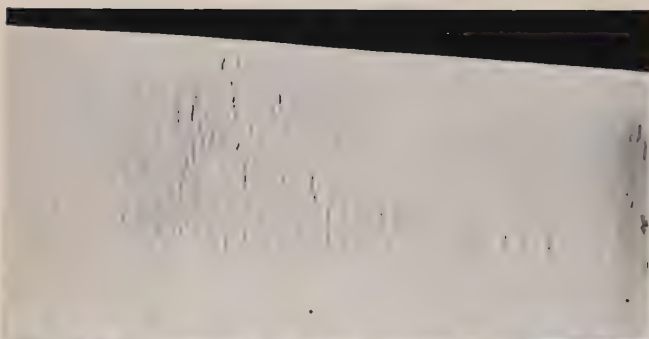
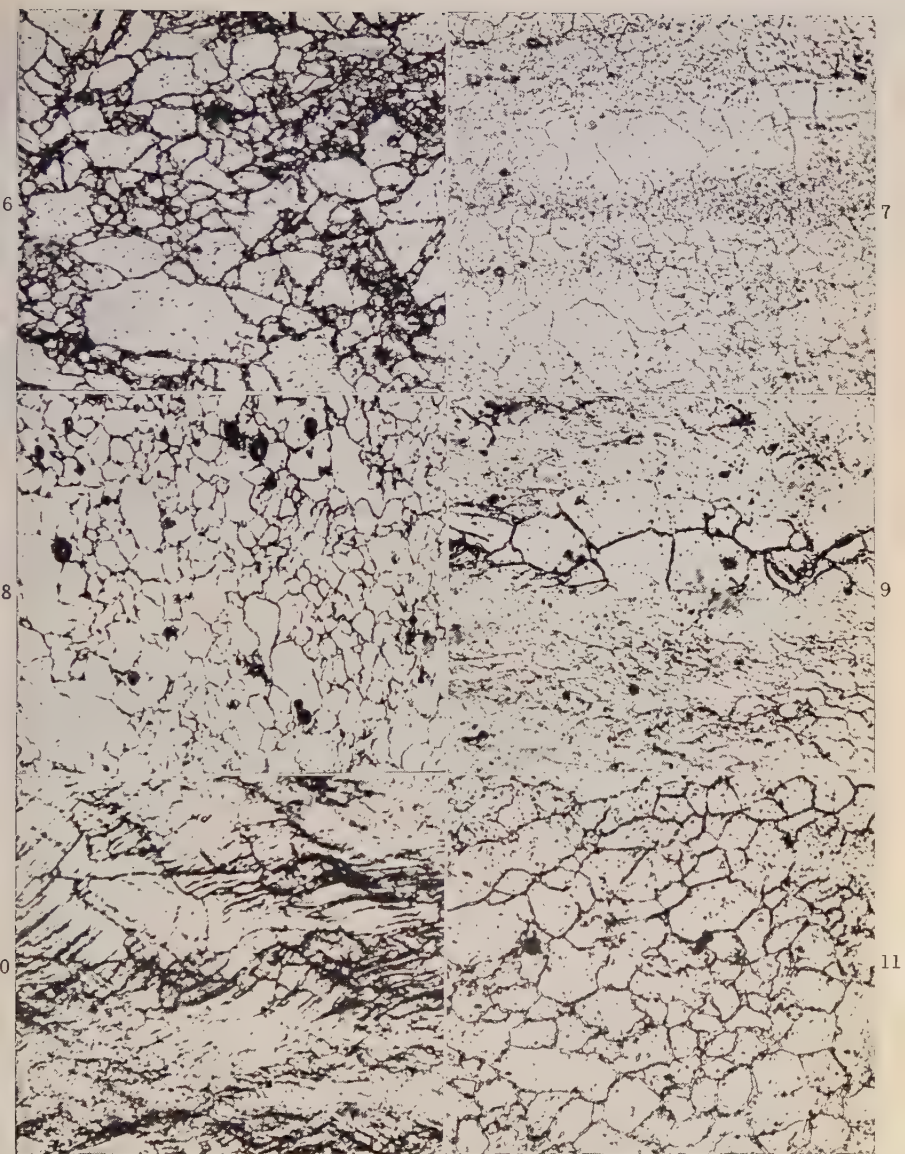


FIG. 5. Fine cracking in reheated magnesium-7% aluminum alloy plate rolled at 450° C.

FIGS. 3-5. Characteristic Types of Rolling Failure.



FIGS. 6-10.—Microstructures of Hot-Rolled Sheet after Various Treatments. $\times 300$

FIG. 6.—8.1% Al. Hot rolled at 350°C .

FIG. 7.—8.1% Al. Hot rolled and annealed at 350°C . for 15 min.

FIG. 8.—5.5% Al. 10% rolling reduction at 400°C .

FIG. 9.—5.5% Al. 30% rolling reduction at 250°C .

FIG. 10.—5.5% Al. 40% rolling reduction at 150°C .

FIG. 11.—Microstructure of Magnesium-7% Aluminium Alloy Sheet Hot Rolled at 400°C . (25% reduction in final stage) showing effect on cold-bending properties. Cold bend = $4.5\ T$. $\times 500$.

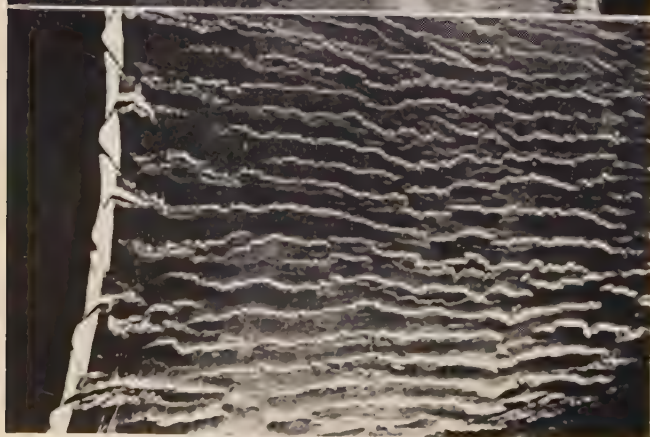


FIG. 3.—Transverse shear cracking in rolled plate.

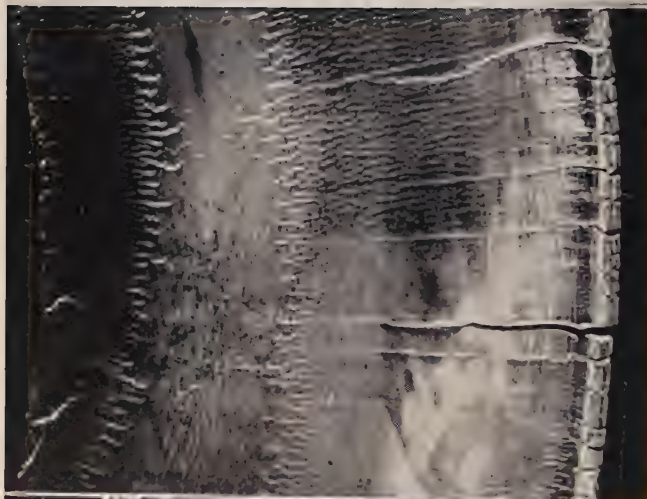


FIG. 4.—Transverse "hot cracking" in reheated magnesium-8% aluminum alloy plate rolled at 450° C.

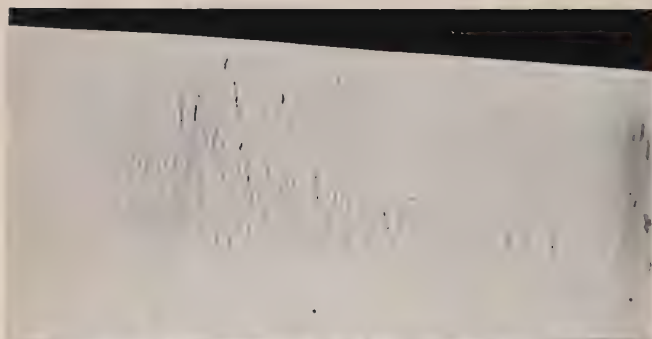
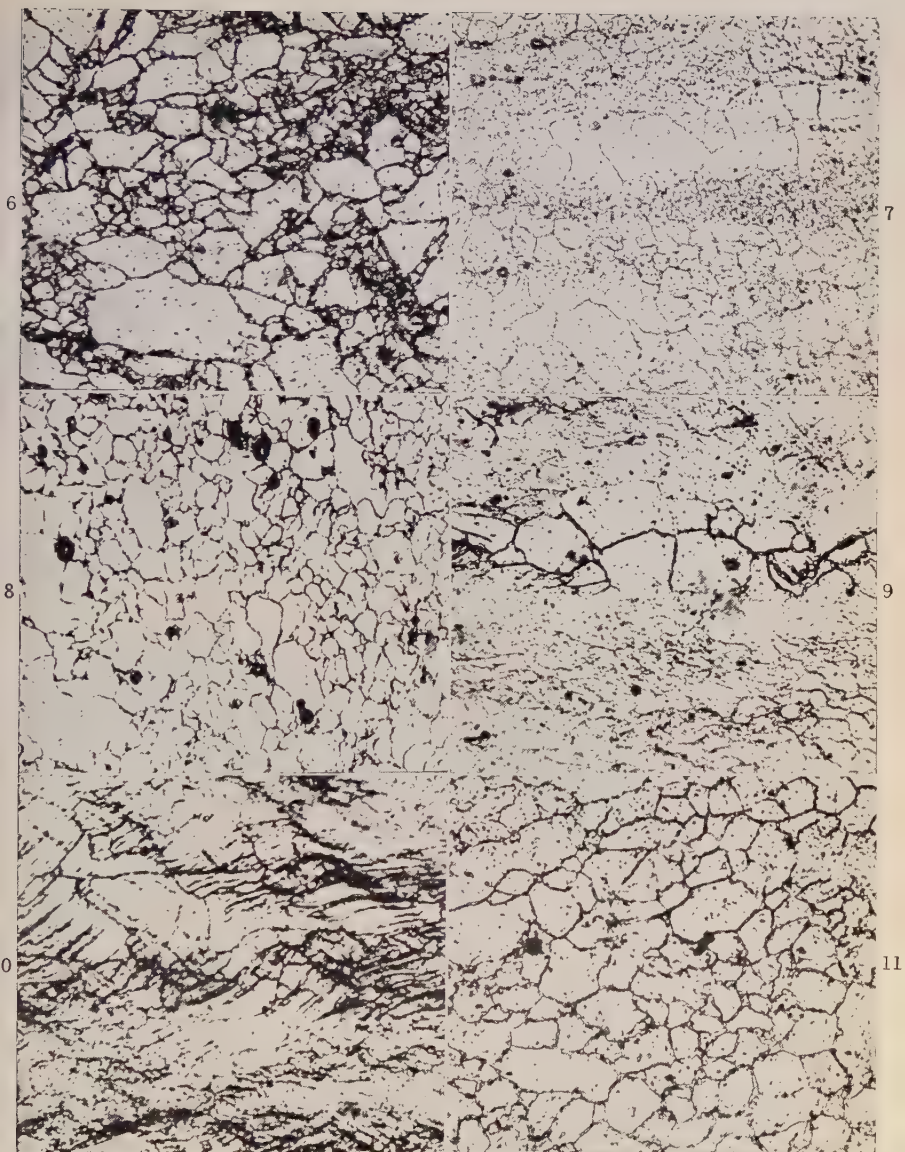


FIG. 5.—Fine cracking in reheated magnesium-7% aluminum alloy plate rolled at 450° C.

Figs. 3-5.—Characteristic Types of Rolling Failure.



FIGS. 6-10.—Microstructures of Hot-Rolled Sheet after Various Treatments. $\times 300$

FIG. 6.—8.1% Al. Hot rolled at 350° C.

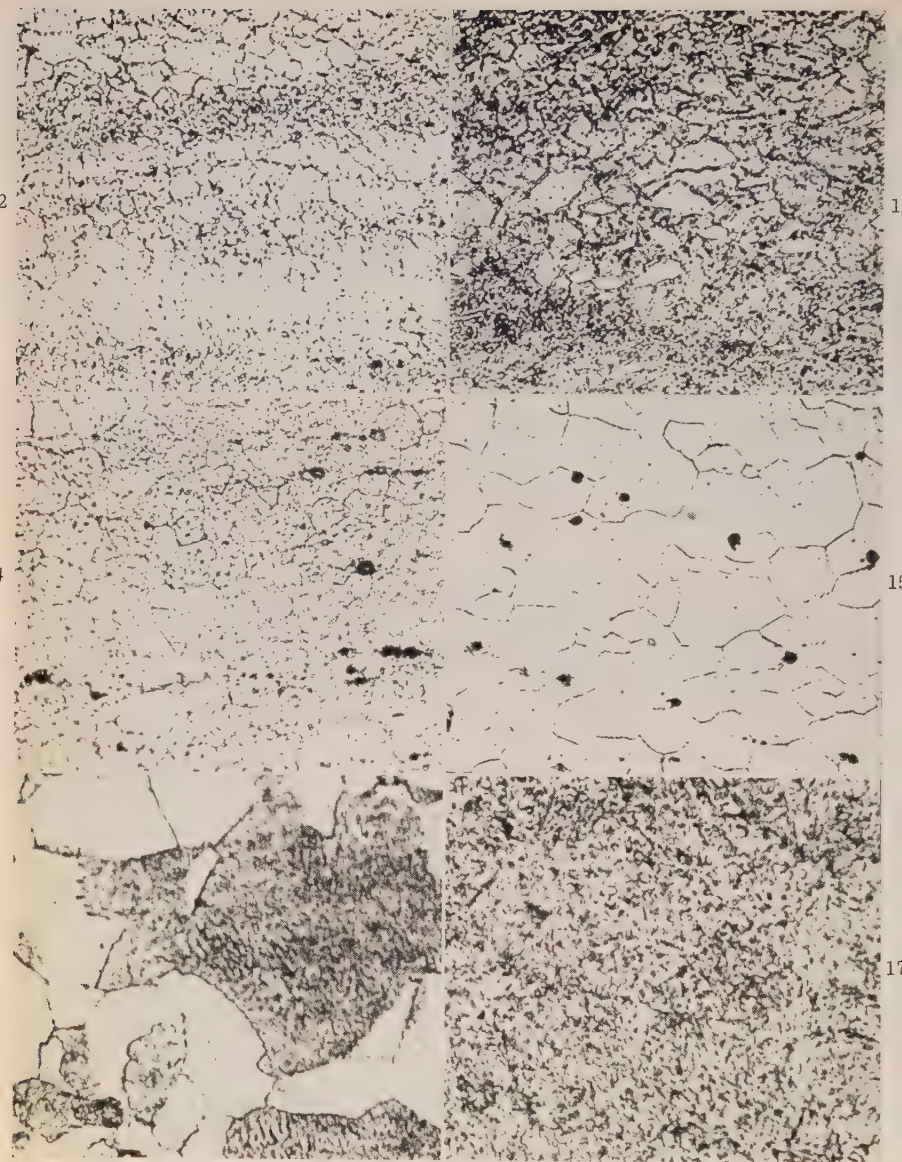
FIG. 7.—8.1% Al. Hot rolled and annealed at 350° C. for 15 min.

FIG. 8.—5.5% Al. 10% rolling reduction at 400° C.

FIG. 9.—5.5% Al. 30% rolling reduction at 250° C.

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FIG. 11.—Microstructure of Magnesium-7% Aluminium Alloy Sheet Hot Rolled at 400° C. (25% reduction in final stage) showing effect on cold-bending properties. Cold bend = 4.5 T . $\times 500$.



FIGS. 12 and 13.—Microstructures of Magnesium-7% Aluminium Alloy Sheet hot rolled from cast ingot without reheating, showing effect on cold-bending properties. $\times 500$.

FIG. 12.—Rolled at 400°C . Cold bend = 5-6 T.

FIG. 13.—Rolled at 450°C . Cold bend = 10 T.

FIGS. 14-17.—Microstructures of Magnesium-Aluminium Alloy Sheets after Various Heat-treatments.

FIG. 14.—7% Al. Annealed at 350°C . for 15 min. $\times 300$.

FIG. 15.—7% Al. Solution-treated at 390°C . for 15 min. $\times 300$.

FIG. 16.—8% Al. Solution-treated and aged at 150°C . $\times 750$.

FIG. 17.—8% Al. Solution-treated and aged at 200°C . $\times 750$.

THE SURFACE CONDITION OF POLISHED ALUMINIUM, WITH A NOTE ON THE EFFECT OF SURFACE SCRATCHES.*

By PROFESSOR E. A. OWEN,† M.A., Sc.D., MEMBER, and Y. H. LIU,† Ph.D.

SYNOPSIS.

An account is given of experiments carried out to investigate by X-ray diffraction the effect of polishing the surface of pure aluminium on different materials, including wash leather, emery paper, aluminium, copper, and zinc. In all cases the surface of pure aluminium, immediately after polishing, assumes the metastable state, in which the lattice parameter is greater than it is in fully annealed material, so that the crystallites in the polished layer are in a state of strain. The stresses remain in the polished surface at room temperature until removed by suitable heat-treatment. The polished layers in the cases investigated were not greater than about 0.1 mm. thick.

The amount of room-temperature recrystallization that occurs after polishing varies with the different polishing materials, and the effectiveness of these materials as polishers of aluminium changes with the nature of the material.

The effect of a single surface scratch on aluminium was also investigated; the recovery curve was found to be similar to the curve obtained with a filed surface. The remote effect of the scratch on the surface of a well-annealed polycrystalline specimen of pure aluminium was found to extend over a distance of at least 1 mm. from the scratch.

I.—INTRODUCTION.

THE nature of polished surfaces has had the attention of both metallurgists and physicists for many years. The problem readily lends itself to examination by electron diffraction, and much valuable information has been obtained by this means. For instance, to mention only one of the many researches conducted in this field, Axon¹ studied polished layers produced on the surface of nickel by different methods of abrasion. He concluded that the depth of amorphous layers created by these abrasive methods is a function of the amount of abrasion and the pressure perpendicular to the surface. Increase of abrasive pressure appears to increase the oxide content in the layers, and this may be due to adsorbed oxygen layers on the metal surfaces and to higher temperatures. This method of investigation deals with the surface, the penetration into the material being very small. Other investigations have been carried out by X-ray diffraction, in which the penetration is greater, and information has been obtained concerning the depth of

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penetration of the effect of polishing. Thus, in an investigation by the back-reflection X-ray method, Vacher² measured the thickness of the cold-worked surface layer resulting from metallographic polishing. He concluded that the thickness of the altered surface layer on aluminium, for example, after different abrasive treatments varied from 5 to 9 microns; he also came to the interesting conclusion that cold-worked layers produced by certain fine-abrasive treatments were thicker than those produced by certain coarse-abrasive treatments. He employed emery powder and aluminium oxide powders of different grades to polish the surfaces. Bénard and Lacombe³ studied by X-rays the nature of the polished surface of a single crystal of aluminium, one of the authors (Bénard⁴) having shown that the X-ray method could be used to explore very small thicknesses of metal. They found that Laue spots obtained with single crystals were replaced by continuous Debye-Scherrer rings when the surface of the crystal was rubbed on emery. These rings showed that the polishing had broken up the surface into crystallites presenting all possible orientations to the X-ray beam. Bénard and Lacombe proceeded to determine the depth of the effect by removing the surface layer in stages by electrolytic polishing, and examining the modifications observed in successive X-ray photographs. They found that the depth of penetration varied between wide limits, according to the abrasive conditions. The Debye-Scherrer rings were, however, very clear and well resolved, and in this respect differed from the rings obtained, say, with iron, which are very diffuse.

The present paper contains an account of a development of some work previously carried out on compressed aluminium,⁵ in which it was found in a few experiments conducted at that time by X-ray diffraction that the polished surface of aluminium exhibited interesting phenomena which, it was believed, had not been previously recorded. As the observations on that occasion had been limited in number, it was decided to extend the scale of the investigation so as to include different kinds of polishing materials. It was also desired to find, if possible, what occurred just below the polished layer. Aluminium was used as the material to be polished because it had previously been found to yield X-ray photographs that could be measured with accuracy; it could also be obtained in a state of high purity. The material used throughout this investigation had a purity of 99.998%, unless otherwise stated.

II.—EXPERIMENTAL PROCEDURE.

The apparatus consisted of a back-reflection camera with which photographs could be taken either when the specimen remained stationary, or when it was simultaneously oscillated and rotated. For the

main purpose of the experiment the camera was used with a stationary specimen. The angle of incidence of the radiation on the surface of the specimen could be varied, but only two angles were in fact used, namely 0° and 30° ; the main work was done with normal incidence. Both cobalt and chromium radiations were employed.

The specimens were in the form of plates about 2 mm. thick and 1 cm. square. The surfaces could be set to within 0.01 mm. over the centre of the camera by means of a reading microscope, and the distance from the specimen to the back of the X-ray film, held firmly in its cassette, was determined with the same template, the length of which was accurately known. The distance from the mid-plane of the film to the specimen must be known accurately when interplanar-spacing values of high precision are required. Two slits were used at different times, to define the X-ray beam; one was 41 mm. and the other 61.5 mm. long, with circular holes 1 mm. in dia. at both ends. The areas of the surface irradiated with these slits were 2.2 and 1.3 mm.², respectively. The distance from the specimen to the film was 54.46 mm. Usually the exposures lasted about 3 hr.

After the specimen had been prepared and its surfaces rendered flat, it was annealed *in vacuo* at 500° C. for 21 days to bring it to the equilibrium state. The polishing operation was started after a photograph had been taken with the material in a state of equilibrium. At first it was considered advisable to polish mechanically by allowing the polisher to pass across the surface of the specimen in the same direction for different lengths of time; the load on the polisher could be varied over a range of pressures as desired. But it was found that, for the immediate purpose, polishing by hand could be regulated more satisfactorily. This method was adopted, the polishing being performed along two approximately perpendicular directions alternately, the number of strokes varying with the nature of the polishing material. Wash leather, fine emery paper (grade 000), aluminium, copper, and zinc were used as polishing materials. Care was taken to ensure that the polishing was done slowly and without applying appreciable pressure, so that the specimens showed no perceptible rise in temperature.

Two circles which could be used as fiducial marks were imprinted on each film. They could be accurately measured and their diameters used to correct for the changes in dimensions of the film which occurred during processing.

III.—EXPERIMENTAL RESULTS.

After the specimen had been annealed at 500° C. for 21 days, a photograph typical of the specimen in the annealed condition was taken.

It showed (see Fig. 9, Plate XXIV) that the specimen consisted of fairly large crystals and gave no indication that there were any very small crystals present, i.e. crystals measuring less than about 10^{-4} cm. across.

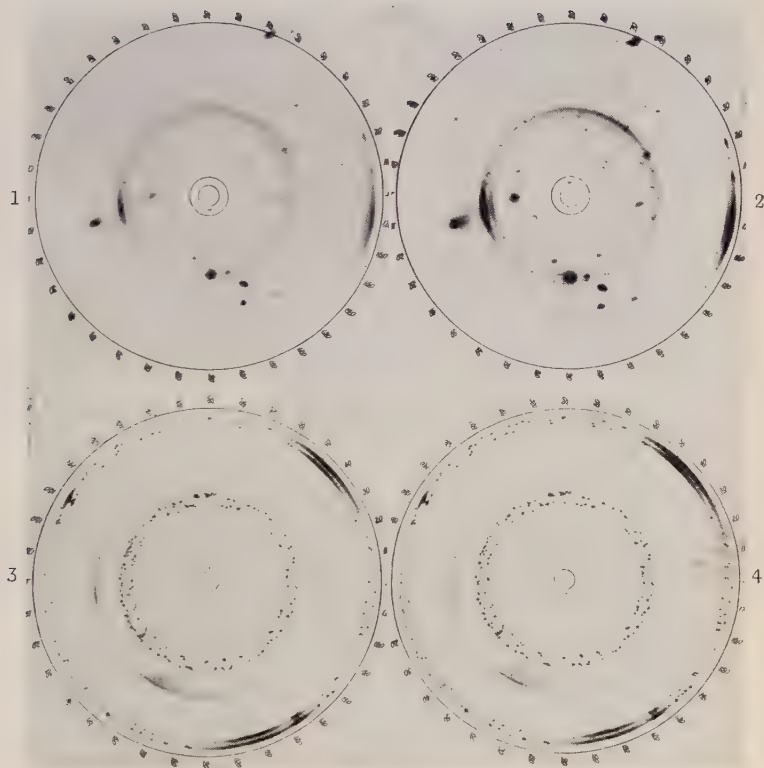
1. *Aluminium Polished on Wash Leather.*

After polishing had been carried out for $\frac{3}{4}$ hr. on wash leather with alcohol as lubricant, a back-reflection photograph showed that some Laue spots had lost their sharp outline. No continuous diffraction rings were observed in the photograph, but those Laue spots in the vicinity of the position that would be occupied by the diffraction rings were drawn out into short arcs along the rings. As the polishing operation proceeded the Laue spots became more blurred and the arcs became more drawn out and intense. The texture, however, remained the same. Even after polishing for 32 hr., no continuous rings, the diameters of which could be measured, were observed in the photograph. The polishing was not carried out for sufficiently long to produce a general breaking up of the surface, but the big crystals which reflected the radiation had their surfaces disturbed sufficiently to cause a deformation of the Laue spots.

2. *Aluminium Polished on Emery Paper.*

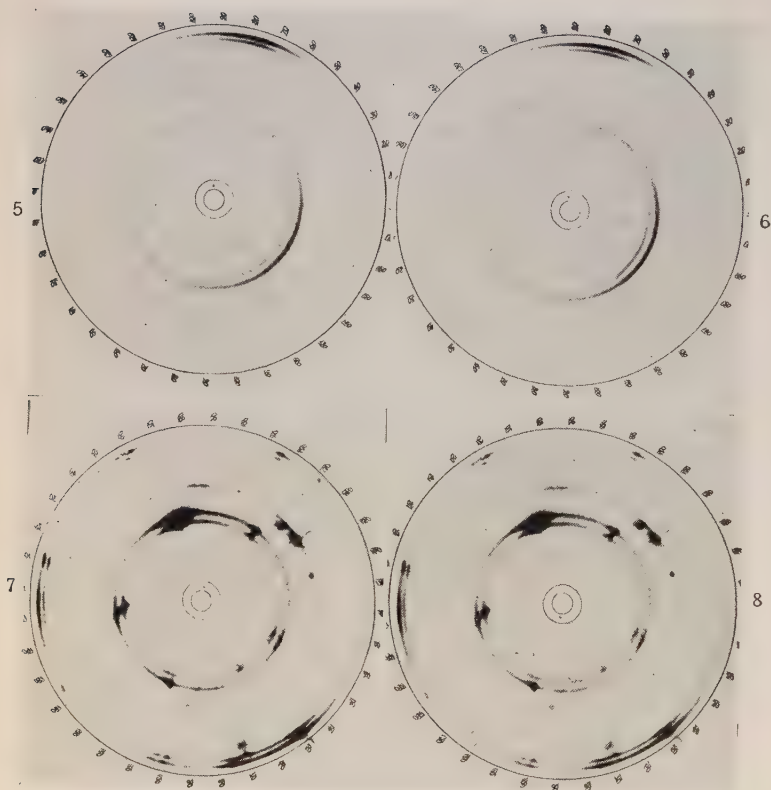
The result of polishing pure aluminium on fine emery paper with alcohol as lubricant is shown in Figs. 1 and 2 (Plate XXXI). In addition to the Laue spots from the larger crystals, produced by general radiation, continuous diffraction rings due to the characteristic radiation of the cobalt target are also present. Half an hour after the polishing was completed, the diffraction rings showed a few spots that were due to recrystallization; the number increased slightly as time passed but soon became stationary. There was, for instance, no difference between the photograph taken after 4 days and that taken after 7 days. In the early stages, immediately after polishing, some degree of recrystallization had undoubtedly occurred, but it was small. The Laue spots present in the original photograph of the annealed plate persisted in varying degrees in all the photographs, showing that the polished layers were very thin, although not so thin that the structures they contained were not recorded on the films. The Laue spots were of about the same relative intensity in each photograph; it is to be noted that the specimen was not moved relative to the incident X-ray beam during all the exposures, of which, in this instance, there were ten taken at fairly regular intervals up to 216 hr.

The measurements of the diffraction rings yielded a constant interplanar spacing, the mean value of which was 0.90364 kX., the



FIGS. 1-4.—Diffraction Patterns, Taken with Co Radiation, of Surface of Pure Aluminium Polished on :

Emery : FIG. 1.— $\frac{1}{2}$ hr. after polishing.
 FIG. 2.—168 hr. after polishing.
 Aluminium : FIG. 3.— $\frac{1}{2}$ hr. after polishing.
 FIG. 4.—241 hr. after polishing.



FIGS. 5-8.—Diffraction Patterns, Taken with Co Radiation, of Surface of Pure Aluminium Polished on :

Copper : FIG. 5.— $\frac{1}{2}$ hr. after polishing.
FIG. 6.—240 hr. after polishing.

Zinc : FIG. 7.— $\frac{1}{2}$ hr. after polishing.
FIG. 8.—168 hr. after polishing.

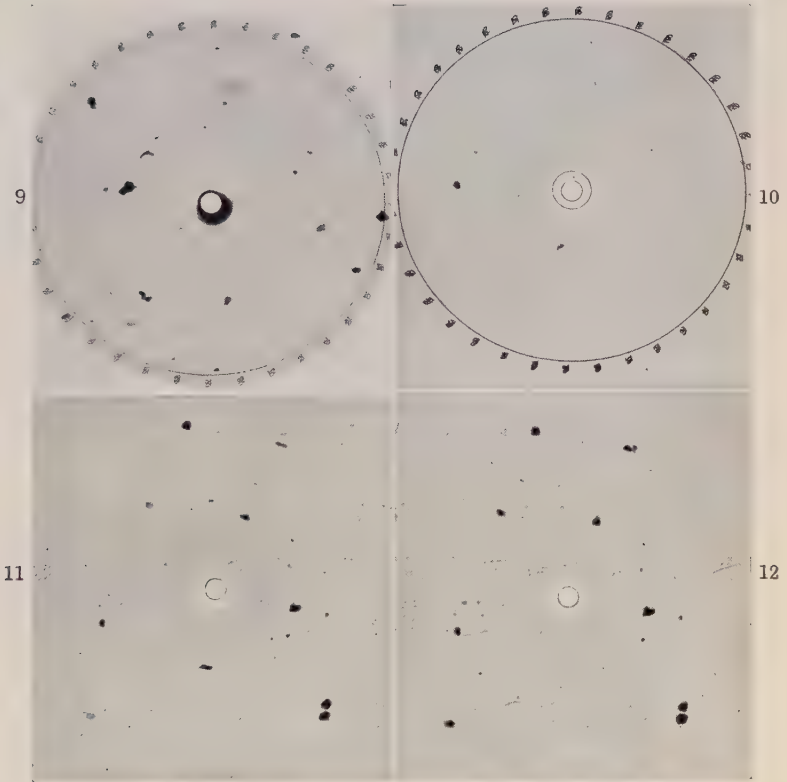
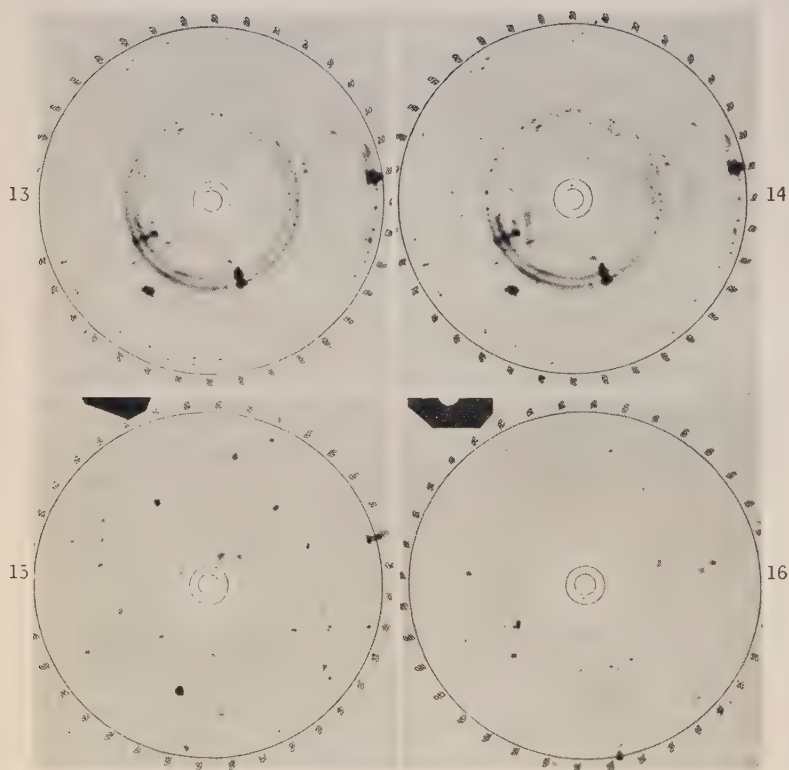


FIG. 9.—Back-Reflection Photograph of the Surface of Annealed Pure Aluminium before Commencing Polishing.

FIG. 10.—Back-reflection photograph obtained with annealed pure aluminium (99.998%).

FIG. 11.—Back-reflection pattern obtained with annealed aluminium of 99.86% purity.

FIG. 12.—Back-reflection pattern of same specimen as Fig. 11 but with a fine scratch on the surface made with a steel needle, showing faint diffraction ring.



FIGS. 13 and 14.—Diffraction Patterns of Surface of Annealed Pure Aluminium (99.998%) $\frac{1}{2}$ hr. (Fig. 13) and 528 hr. (Fig. 14) after deep scratch had been made across irradiated area.

FIGS. 15 and 16.—Diffraction patterns of same surface as Figs. 13 and 14 taken 1 mm. (Fig. 15) and 2 mm. (Fig. 16) from scratch.

interplanar-spacing value of the (420) planes of aluminium when in the metastable state. The lattice parameter corresponding to this spacing, assuming that the material behaves isotropically in the metastable state (as there is reason to believe it does), is 4.0412_0 kX. This remained the same whether the X-ray beam fell normally on the surface or at an angle of incidence of 30° . Reflections from the (222) planes with chromium radiation yielded the same lattice parameter as did the reflections from the (420) planes with cobalt radiation. After the specimen had been annealed, the lattice parameter was found to be 4.0406_5 kX., the equilibrium value.

It was not considered satisfactory to accept these results without further tests, as some impurities from the emery might have entered the surface and vitiated the parameter values. The work was therefore continued with two surfaces of aluminium.

3. Aluminium Polished on Aluminium.

The specimens were annealed at 500° C. for 21 days. In their original state the plates, after annealing, contained large crystals. The pure specimen under observation was polished on a sheet of aluminium of 99.96% purity, using alcohol as lubricant. The surface layer on the aluminium sheet was etched off with dilute hydrofluoric acid and the new surface washed with alcohol. Both specimen and sheet were kept in a desiccator for a few days before use.

Photographs of the same spot on the surface of the specimen were taken at different times after polishing; two samples are reproduced in Figs. 3 and 4 (Plate XXII). The radiation (cobalt) fell at normal incidence on the polished surface. Measurements of the continuous diffraction rings showed that the interplanar spacing was constant, yielding a lattice parameter the mean value of which was 4.0412_3 kX. at 18° C., i.e. the metastable value. All the photographs were identical, the pattern of spots in the photograph taken half an hour after polishing being the same as that taken after 10 days (Figs. 3 and 4). The characteristics of the photographs were somewhat different from those obtained with aluminium polished on emery paper. Whereas with emery paper there were very few spots and pronounced continuous diffraction rings, with aluminium as polisher the spots were very numerous and the continuous diffraction rings far less pronounced.

4. Aluminium Polished on Copper.

An attempt was now made deliberately to introduce impurity into the aluminium lattice by polishing on a copper sheet. The copper sheet (99.94% pure) was cleaned with dilute nitric acid and kept in a

desiccator for a few days before the polishing operation. The specimen, as in the previous cases, was polished with great care, as little pressure as possible being applied, so that a surface smooth and free from visible scratches resulted. Alcohol was again used as lubricant. Chromium and cobalt radiations were used in turn, and the angle of incidence of the X-ray beam on the surface was varied. The back-reflection photographs were very different from those obtained after polishing either with emery paper or with aluminium. They now consisted of continuous diffraction rings showing preferential orientation amongst the crystallites produced in the polishing operation (Figs. 5 and 6,

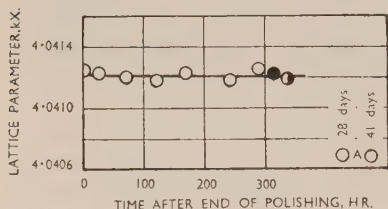


FIG. 17.—Change of lattice parameter with time after polishing for aluminium polished on copper.

KEY.

- (420) reflections, Co radiation, normal incidence.
- ◐ (420) reflections, Co radiation, angle of incidence 30°.
- (222) reflections, Cr radiation, normal incidence.

Plate XXIII); there were very few sharply-defined spots on the diffraction rings compared with the number observed in the photographs of specimens polished on emery or aluminium. During polishing the surface crystals had been broken up into crystallites of a size less than 10^{-4} cm. There were no big crystals and only a slight indication of recrystallization having occurred at any time during or after polishing within a period of 10 days.

The diffraction rings were measured with the results shown in Fig. 17; the lattice parameter was found to be constant, the mean value being 4.0412_0 kX., which is characteristic of the metastable state. It was expected that the polished layer would dissolve some of the copper. Any copper atoms picked up by the aluminium would be concentrated in the surface layer and would probably not enter the body of the material at room temperature. No indication of the presence of copper in the aluminium was found in the photographs taken. After it had remained at room temperature for 26 days without change in lattice parameter, the specimen was raised to a high temperature to facilitate the diffusion of copper if it were present; the specimen was annealed for 2 days at 500° C. and water-quenched. The back-reflection photographs taken with the originally polished surface 1 hr. and 13 days, respectively, after quenching gave the lattice-parameter values 4.0406_7 and 4.0406_8 kX. (shown at A in Fig. 17), the equilibrium value of pure aluminium. No detectable amount of copper had therefore entered the aluminium lattice during the polishing operation.

5. *Aluminium Polished on Zinc.*

To investigate further the possible entry of foreign atoms into the polished surface, the aluminium was polished on zinc, as this might prove more active than copper. The same procedure as with other polishing materials was followed. Two specimens of the back-reflection photographs taken are shown in Figs. 7 and 8 (Plate XXIII). The series included exposures made on the same spot of the specimen's surface over a period extending from half an hour to 168 hr. after polishing was completed. As in the previous case, the polishing resulted in the production of a large number of crystallites giving rise to complete diffraction rings and to distorted crystals in the surface of the specimen (Figs. 7 and 8). As with copper, there is little indication of recrystallization having taken place, or of the big crystals having been broken up into crystals of sizes greater than 10^{-4} cm. which would be free from particle scattering. The complete diffraction rings due to the crystallites produced by polishing again yielded a value of the lattice parameter corresponding to the metastable state of aluminium. When the polished specimen was annealed at 400° C. for 2 days and water-quenched, it gave the equilibrium parameter value of 4.0406_5 kX. This value did not change when the specimen was further annealed for a period of 36 hr. at 500° C.

Although the measurements made on annealed specimens after polishing on copper or zinc indicated that atoms of these elements had not entered the crystal lattice of aluminium, it must be borne in mind that the atoms, if present, would be concentrated in the amorphous layer to a depth not exceeding about 30–100 Å. As the result of atomic diffusion during annealing, the concentration of the solid solution would be so small that the change in parameter might not be detected by the X-ray method. The conclusion from the foregoing results is that the amount of impurity picked up during polishing, as carried out in these experiments, is so insignificant that it does not affect the lattice spacing to a measurable degree.

6. *Electrolytic Etching of Polished Surfaces.*

A lightly polished specimen which had been in the equilibrium state before polishing but which was now in the metastable state, was etched electrolytically in a perchloric acid-alcohol bath. After etching, which removed a layer about 0.1 mm. thick from the surface, the interplanar spacing yielded the equilibrium value 0.9035_1 kX., corresponding to the lattice parameter 4.0406_5 kX., and the texture was that of fully annealed aluminium. Thus, only a surface layer, not greater than 0.1 mm. thick, was in this case affected by the polishing process,

IV.—CONCLUSIONS.

Although differing in detail, the essential features of the back-reflection photographs of all the polished surfaces were the same. The Laue spots were slightly blurred after polishing and some were associated with short arcs; this was particularly marked when the Laue spots were near the diffraction rings. Each photograph showed continuous rings due to small crystals less than 10^{-4} cm. in size; the lattice parameter calculated from measurements of these rings was found in each case to be that corresponding to the metastable state of aluminium, the value remaining constant until the specimen was again annealed at a high temperature. After polishing on zinc or copper there was little, if any, indication of recrystallization; with aluminium as polisher the diffraction rings were covered with spots, indicating the presence of small crystals, and the patterns were the same in all the photographs taken. In this case it is possible that in the polishing operation the surface crystals were broken up into crystals of sizes varying over a wide range, those bigger than 10^{-4} cm. giving the spots and those of smaller dimensions giving the faint continuous diffraction rings; in addition, a certain amount of recrystallization may have occurred during or immediately after polishing, resulting from the cold work done on the material. With an emery-paper polisher a slight amount of recrystallization definitely occurred in the initial stages after polishing.

Since the surface of pure aluminium, when polished on emery, aluminium, copper, or zinc, immediately assumes the metastable state, the lattice parameter being then greater than in the normal fully-annealed material, the crystallites in the surface are in a state of strain. The residual strains remain in the polished surface at room temperature and are not removed until the material is suitably heat-treated.

Bowden and Hughes ⁶ in a study of the physical properties of surfaces after polishing found that the process of polishing is greatly influenced by the relative melting-points of the polisher and the material polished. Their experiments suggest that an important factor in the polishing process is intense local heating of the solid surfaces at points of contact, causing softening or melting followed by rapid cooling due to the liquid used as lubricant. The molten metal flows over the surfaces, forming the Beilby layer. Experiment showed that if the polisher melts or softens at a lower temperature than the material polished, the former will melt and flow first, and will have comparatively little effect on the surface of the latter. Provided, however, that the melting point of the polisher is higher than that of the material polished, surface flow, polish, and the formation of the Beilby layer readily occur on the polished material,

Figs. 3-8 (Plates XXII and XXIII) show that the back-reflection X-ray diffraction patterns obtained with aluminium surfaces rubbed on pure metal surfaces, vary with the nature of the polisher. When aluminium is rubbed on aluminium both surfaces suffer similar changes if melting occurs at the points of contact. In this case rapid recrystallization develops, as evidenced by the numerous spots observed on the diffraction rings, but in addition particle-scattering and diffraction by distorted surface crystals take place, both of which produce continuous diffraction rings. The diffraction effects from these last two causes are small, however, because in the photographs (Figs. 3 and 4) the continuous rings are of low intensity, and a part at least of this intensity must be due to crystals, formed by recrystallization, that are too small to produce regular reflection of the X-rays.

When aluminium is rubbed on copper, on the other hand, the predominant feature of the photographs (Figs. 5 and 6) is the production of continuous diffraction rings by particle-scattering and distorted surface crystals; recrystallization giving rise to crystals large enough to produce regular reflection is almost entirely absent. Some factor in the polishing process on copper inhibits the growth of crystals by recrystallization. But copper produces on aluminium a better polish than does aluminium. Furthermore, the surface layer produced with copper is thinner than that produced with aluminium, judging by the intensity and the number of Laue spots from the body of the material appearing in the photographs.

With zinc, the polished layer appears to be even thinner than with copper, and the photographs (Figs. 7 and 8) supply ample evidence of the presence of distorted surface crystals. As with copper, there is but little evidence of the occurrence of recrystallization. It seems, therefore, that the difference between copper and zinc as polishers of aluminium is that the former produces a deeper surface layer than the latter when the amount of work expended in the polishing process is approximately the same, but the production of crystals, by recrystallization, large enough to produce regular reflection of the X-rays, is practically absent with both metals. These results are directly contrary to the results obtained with aluminium. Although zinc produces a polish on aluminium, it is not as effective as copper in this respect, but both copper and zinc appear to be better than aluminium as polishers of aluminium. No contamination of the aluminium surface when rubbed on copper or zinc was detectable.

There seems to be some measure of agreement with the results of Bowden and Hughes, especially when aluminium or copper is used as polisher, but certain results obtained with zinc, namely, that it polished

aluminium and that no zinc contamination of the polished aluminium surface could be detected, are difficult to reconcile with their views. It would be well to examine the aluminium surface after polishing on zinc by electron diffraction, which may be more sensitive than the X-ray method here employed, to small amounts of contamination.

It has been seen that the effects produced by rubbing aluminium on the pure metals aluminium, copper, and zinc differ among themselves, but they all differ from the effect produced by rubbing on emery. Figs. 1 and 2 (Plate XXII) provide definite evidence of recrystallization which is not so rapid as that observed with aluminium as polisher, when recrystallization occurs and ends during the polishing operation or very soon after it is completed. It may be argued in this connection that the surface of aluminium rubbed on aluminium gets broken up into smaller crystals without distortion, but the evidence from all the photographs is that distortion of the surface crystals accompanies the polishing operation. We may, however, be wrong in attributing the spots on the rings in Figs. 3 and 4 entirely to recrystallization. Some may be due to fragmentation of surface crystals without distortion, but the weight of evidence from the photographs taken as a whole is against this conclusion.

APPENDIX.

NOTE ON THE EFFECT OF SURFACE SCRATCHES.

In the above study of polished surfaces, mechanical polishing was not adopted because it was difficult so to regulate it that no scratches were produced in the operation. Hand polishing was therefore resorted to so as to avoid scratches and so that the surface could be observed frequently. An account will now be given of a few experiments performed to study in the first instance the effect of scratching the smooth surface of an annealed specimen of aluminium of 99.86% purity. Fig. 11 (Plate XXIV) shows a back-reflection photograph of the specimen in its initial annealed state; it consists of some large crystals and several smaller ones, but there is not a large number of very small crystals such as would yield continuous rings similar to those found in compressed material. With the sharp point of a steel needle a fine scratch was made on the surface, passing across the irradiated area. The back-reflection photograph subsequently taken is shown in Fig. 12 (Plate XXIV). A close scrutiny of this photograph reveals the presence of the outline of a fine circle which was very distinct only over one section of the circumference. This diffraction ring was in the posi-

tion where it would be expected with the radiation employed if the scratch produced a large number of crystallites small enough to produce particle-scattering as in the photographs taken with compressed material. The diffraction rings were too faint for measurement.

A deeper scratch was then made on the surface of a specimen of annealed aluminium (99.998% pure), the initial state of the surface being as shown in Fig. 10 (Plate XXIV). The back-reflection photographs of the specimen after making the scratch on the surface showed complete diffraction rings dotted over irregularly by small spots indicating recrystallization and the breaking up of the surface crystals. The characteristics of these photographs were much the same as those of the photographs obtained with

aluminium polished on aluminium. Photographs (two of which are shown in Figs. 13 and 14, Plate XXV) were now taken at different intervals after making the scratch, using both cobalt and chromium radiations in turn and allowing the radiation alternately to fall normally on the surface and at an angle of incidence of 30° . The measurements of these photographs yielded the curve shown in Fig. 18. In this curve the initial lattice parameter is low; in course

of time it increases to a constant value corresponding to the metastable state. The curve is of the same form as the recovery curve observed with a filed surface.¹ This can readily be understood, since filing is really vigorous scraping or scratching of the surface.

In order to investigate the stress penetration due to scratching, regions of the surface 1 and 2 mm. away from the scratch were examined by X-ray diffraction. Both back-reflection photographs taken (Figs. 15 and 16, Plate XXV), yielded continuous rings, the areas of the irradiated regions being shown as the black circular spots on the top left-hand corners of the photographs. Owing to the faintness of the lines it was impossible to make any measurements. However, the photographs indicated that the stress due to the scratch extended over a distance of at least 1 mm. from the scratch in this particular case. The distance of

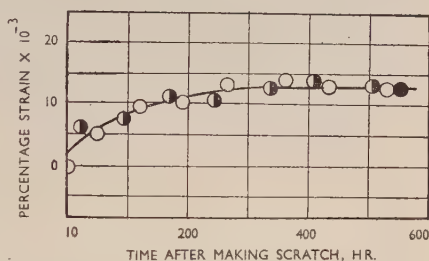


FIG. 18.—Showing how the percentage strain $\left(\frac{d_{\text{obs.}} - d_{\text{eq.}}}{d_{\text{eq.}}} \right) 100$ produced by a deep scratch on the surface of pure aluminium changes in course of time.

KEY.

- (420) reflections, Co radiation, normal incidence.
- ◐ (420) reflections, Co radiation, angle of incidence 30° .
- (222) reflections, Cr radiation, normal incidence.

stress penetration will depend on the pressure applied to make the scratch, the crystal size, and the purity of the specimen. The effect of the stress may be perceptible at greater distances in single crystals of pure metals, as no crystal boundaries would then be present to obstruct the propagation of the stress. Since the effect of a scratch made on the surface of a polycrystalline specimen can be detected on the surface at least 1 mm. away from the scratch, it must be concluded that below the scratch its effect will also be felt over an appreciable depth.

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CAST STRUCTURES IN SUPER-PURE AND 1272 COMMERCIALLY PURE ALUMINIUM.*

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SYNOPSIS.

The macrostructures of cast super-pure and commercially pure aluminium have been correlated with : (a) the degree of superheating of the metal, (b) the rate of cooling, and (c) turbulence in the metal during the filling of the mould. With super-pure aluminium the cast macrostructure is closely related to the heating and cooling cycle of the molten metal. In the case of commercially pure aluminium there is a range of superheating temperatures, approximately up to 20°–25° C. above the liquidus, in which residual nuclei are the principal factors responsible for the cast structure obtained. These nuclei were found to contain small amounts of titanium. Foreign nuclei play the greatest part in refining the grain-size of the two grades of aluminium used ; mechanical disturbance is not so effective, and increasing the rate of cooling is least effective.

I.—INTRODUCTION.

THE term " cast structure " is taken in this paper to mean the size and shape of primary crystals formed during solidification. These two properties of the grains, which may be made visible by macro- or microscopic methods, play an important part in the subsequent behaviour of the cast metal, when it is exposed to different conditions of stress, temperature, or other physical or chemical influences.

The origin of cast structures in metals and alloys is both a physico-chemical and a metallurgical problem. When examined from a theoretical standpoint, the origin of such structures resolves itself into a question of explaining the number and size of grains in terms of two fundamental phenomena of crystallization, viz. the rate of nucleation of crystals and the rate of crystal growth. This classical approach is essentially that of Tammann,¹ who also held that these two fundamental phenomena could be related to certain physical and chemical properties of the metal on the one hand and to the metallurgical factors of melting and casting on the other. Unfortunately, great experimental difficulties are encountered in measuring either of the two rates in liquid metals. Consequently, the great bulk of work on cast structures has been indirect. The number and size of grains in cast metals have been studied as functions of either physical or metallurgical variables, and the results

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related and explained, whenever this has proved possible, in terms of the fundamental phenomena as propounded by Tammann.

The work described in the present paper forms part of a comprehensive investigation of cast structures. In this preliminary work, cast structures in super-pure and commercially pure aluminium are correlated with certain metallurgical factors, mainly with the thermal history of the molten metal, the thermal gradients existing during cooling, and mechanical effects which may arise during pouring. It is believed that such data as have been obtained are necessary for the understanding of the phenomena of solidification and may prove helpful in any more fundamental study of the problem.

II.—OUTLINE OF PREVIOUS WORK.

The shape of a crystal grain in a metal casting may be one of two types, equi-axed or columnar. The equi-axed crystals may be either microscopic or macroscopic in size; the columnar crystals are generally macroscopic. One and the same casting may show different sizes of equi-axed grains, as well as both equi-axed and columnar crystals in different zones. Most of the past work on the subject of cast structures has aimed at explaining the origin of these types of cast crystals, their number, and their distribution.

According to the current theories, the number of grains is chiefly determined by the condition of the liquid metal just above the solidification temperature.^{2,3} The liquid may already contain foreign nuclei suitable for promoting crystal growth, in which case fine equi-axed crystals are obtained throughout the mass. Alternatively, in the absence of such nuclei, the liquid crystallizes by generating its own or kindred nuclei, the number of grains in this case being mainly determined by the rate of cooling and the chemical composition of the alloy.^{4,5} Conditions leading to undercooling favour greater rates of kindred nucleation and finer cast structures.⁶ Kindred nucleation may be effected by physical (e.g. electromagnetic) or mechanical forces (vibrations).⁷ Turbulence during pouring may carry suitable nuclei from one part of the casting to another and also modify the temperature gradients during cooling.⁸

The addition of solute atoms generally has a grain-refining effect on the cast structure.^{4,5} The change in rates of nucleation in metallic solutions can be related to the atomic characteristics of the metals concerned; this particular aspect has been studied chiefly by Northcott.⁵

The distribution of grains within the casting has been found to be mainly dependent on the direction and magnitude of temperature gradients existent during solidification, and on the chemical composition

of the alloy. Fine ("chilled") equi-axed crystals at the surface of a casting are believed to be mainly due to surface undercooling effects.⁸ The presence or absence of columnar crystals in a casting depends on the magnitude of the temperature gradients set up and on the presence of the required amount and type of solute atoms;⁵ the greater the temperature gradient, the greater is the tendency to columnar growth. In addition, any of the factors mentioned above as affecting the number of nuclei, may at the same time affect the distribution of different types of crystals.

A considerable amount of experimental data on cast structures is available in the metallurgical literature. The greater part of these data is qualitative in nature and does not lend itself to a theoretical examination of the whole problem. For this reason, more systematic investigations of the effects of metallurgical factors on cast structures

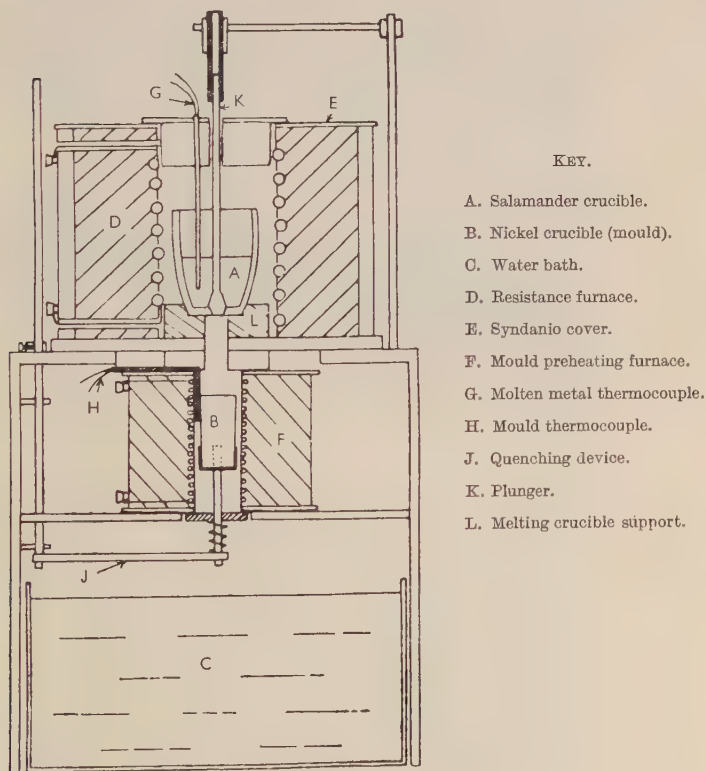


FIG. 1.—Schematic Representation of Non-Turbulent Casting Apparatus.

are still required. One of the objects of the present work is to provide quantitative data which may be found helpful in a theoretical examination of the subject.

III.—THE APPARATUS AND EXPERIMENTAL RESULTS.

The principal variables investigated in the present work were: (a) the temperature of superheating and pouring, (b) the rate of cooling, and (c) mechanical disturbances during filling of the mould. For studying

the effect of thermal factors, the apparatus shown in Fig. 1 was used. Pre-melted and degassed ingots (1 lb.) were remelted in an alumina-coated Salamander crucible (*A*) held in a resistance furnace (*D*); after the desired thermal cycle had been accomplished the metal was poured, by lifting the plunger (*K*), into a nickel crucible (*B*) (2 in. in dia. and 4 in. long) held at the temperature of the molten metal in a furnace (*F*) directly under the melting furnace. The nickel crucible was then cooled either by immersing it (up to the top level) in a water bath (*C*), or by allowing solidification to take place in air. The temperature of the metal in the melting furnace was measured by means of a Chromel/Alumel thermocouple lightly coated with alumina (*G*) with an

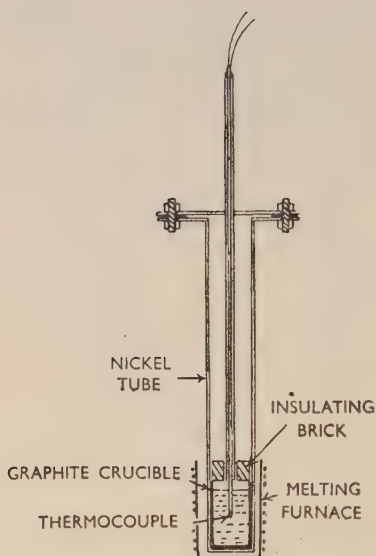


FIG. 2.—Apparatus for Measurement of Undercooling.

accuracy of $\pm \frac{1}{2}^{\circ}$ C. The thermal gradients set up during cooling of the metal in the nickel crucible were determined by continuously recording the temperature with a fast recorder, having maximum deflection response of 0.2 sec. For this purpose, two 24-gauge Chromel/Alumel thermocouples were inserted, one $\frac{1}{8}$ in. from the bottom and the other in the centre of the nickel crucible.

For a range of lower rates of cooling, the device shown in Fig. 2 was used. The metal was held in a graphite crucible (1 in. \times 3 in.) and melted by holding the nickel tube in the melting furnace. After the desired thermal treatment, the nickel tube was lowered into the cooling medium and the metal allowed to solidify.

SUPER-PURE ALUMINIUM.



FIG. 3.—Slow Quiescent Solidification from 670° C.

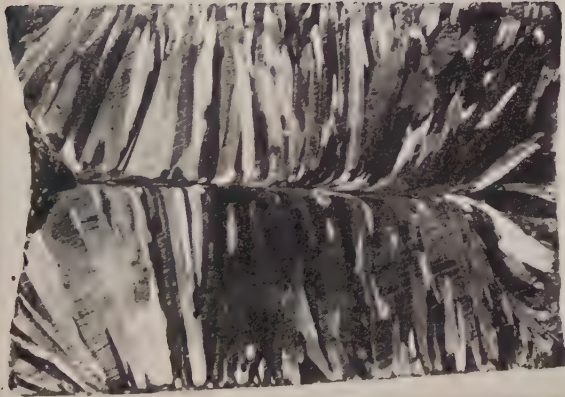


FIG. 4.—Rapid Quiescent Solidification from 670° C.

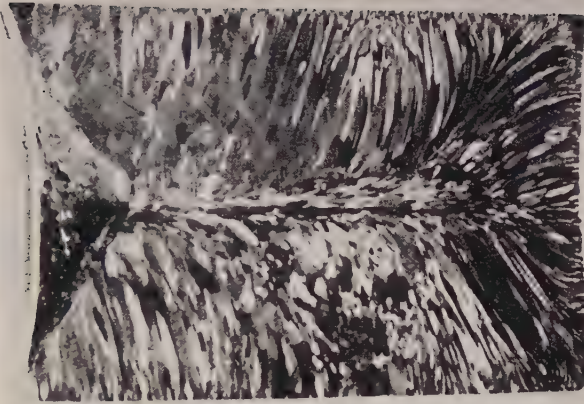


FIG. 5.—Rapid Turbulent Solidification from 670° C.



FIG. 6.—Slow Quiescent Solidification from
670° C.





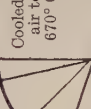
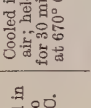
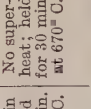

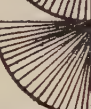

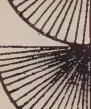



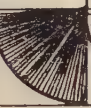




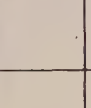




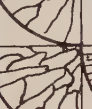
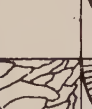





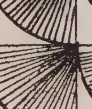
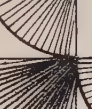

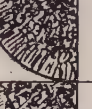









FIG. 7.—Rapid Quiescent Solidification from
670° C.



FIG. 8.—Rapid Turbulent Solidification from
670° C.

TABLE I.—Effect of Process Variables on Cast Macrostructure.

Metal	Type of Solidification	Cooling Medium	Pouring Temperature, ° C.					Superheating Temperature : 950° C. Pouring Temperature : 670° C.	
			670	685	710	760	860	Cooled in air to 670° C.	Cooled in air; held for 30 min. at 670° C.
Super-Pure Aluminium	Quiescent	Air							
		Water							
	Turbulent	Water							
		Air							
Commercially Pure Aluminium	Quiescent	Water							
	Turbulent	Water							

The effect of mechanical disturbances arising during the filling of a mould was studied by casting suitably-treated molten aluminium directly into the nickel crucible held in a water bath.

Two grades of aluminium were used throughout: (a) super-pure aluminium containing iron 0.0005, silicon 0.001, copper 0.005, and aluminium 99.998%; and (b) commercially pure aluminium containing iron 0.25, silicon 0.14, magnesium 0.026, copper 0.013, titanium 0.019, and aluminium 99.552%. Pre-melting, degassing with hexachlorethane, and ingotting were employed in order to ensure uniformity of the stock. Cast ingots were cut vertically through the centre line or horizontally at half height and etched in cupric chloride solution.

The effects of the melting, superheating, and pouring temperatures on the cast macrostructure of super-pure and commercially pure aluminium are shown in Table I. The sketches correspond to quadrants of horizontal sections of the ingots and the grain-size variation is approximately that observed in actual castings. Table I indicates the trends in grain-size rather than the actual number of grains observed. A selection of photomicrographs illustrating the main points observed is given in Figs. 3-8 (Plates XXVI and XXVII) reproduced at slightly less than actual size.

In addition to the experiments whose results are condensed in Table I, others were carried out to determine the effect of repeated melting

TABLE II.—*Cooling Rates and Temperature Gradients in Cast Aluminium.*

Material	Method of Cooling	Metal Temp., ° C.	Rate of Cooling to the Freezing Point, ° C./sec.	Temp. Gradient (° C.) Measured by two Thermocouples just before Solidification	Degree of Undercooling (° C.), $\frac{1}{2}$ in. below the Surface
Super-pure aluminium.	Air, quiescent.	680 or 750	} 1.25	4 {	$\frac{3}{4}$ -1 1 $\frac{1}{4}$ -2
	Water, quiescent.	680 or 750	50 (on the surface), 10 ($\frac{1}{2}$ in. below the surface), 2-5 (1 in. below the surface).	25-30	4-5
	Water, turbulent.	750	5 ($\frac{1}{2}$ in. below the surface), 2 (1 in. below the surface).	2.5	Not measurable.
Commercially pure aluminium.	Air, quiescent.	680	As with s.p. aluminium.	As with s.p. aluminium.	0
	Air, quiescent.	750	As with s.p. aluminium.	As with s.p. aluminium.	As with s.p. aluminium.

and of degassing on the cast macrostructure. Starting with charges differing widely in the fineness of their macrostructures, super-pure aluminium, melted and poured from a constant temperature, gave the same macrostructure, irrespective of the initial grain-size. Identical results were obtained with commercially pure aluminium. Degassing of both grades of aluminium at 665° or 850° C., with 0.5% by weight of the charge of C_2Cl_6 , had no effect on the macrostructure. No experi-

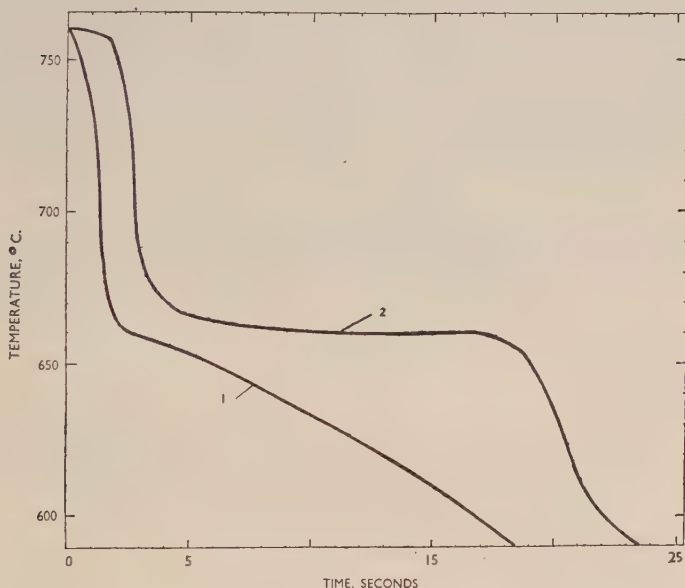


FIG. 9.—Rapid Quiescent Solidification of Super-Pure Aluminium from 760° C.

Curve 1. Thermocouple $\frac{1}{8}$ in. from surface of specimen.
 „ 2. Thermocouple in centre of specimen.

ments were carried out, however, on the effect of intentionally saturating the metal with a soluble gas, and the above experiments were intended only as a check on the experimental procedure.

Temperature measurements made during the casting of either grade of aluminium from 680° or 750° C. and quiescently cooling in either air or water, or turbulently cooling in water, were used to obtain the cooling rates and gradients existing during solidification, as well as the temperatures of undercooling. These results are summarized in Table II. The degree of undercooling could be measured readily for air and slow rates of cooling, and was just detectable for water rates of cooling.

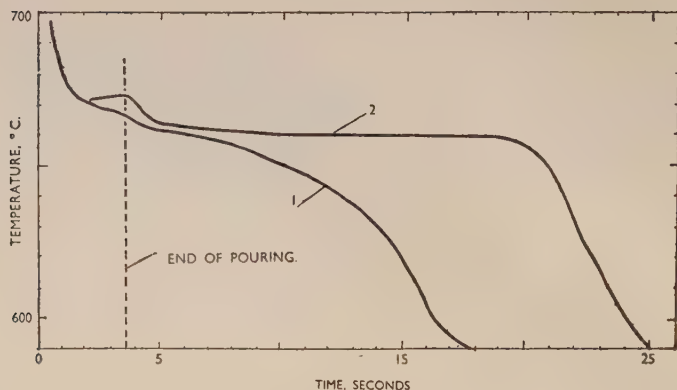


FIG. 10.—Rapid Turbulent Solidification of Super-Pure Aluminium from 760° C.

Curve 1. Thermocouple $\frac{1}{8}$ in. from surface of specimen.
 „ 2. Thermocouple in centre of specimen.

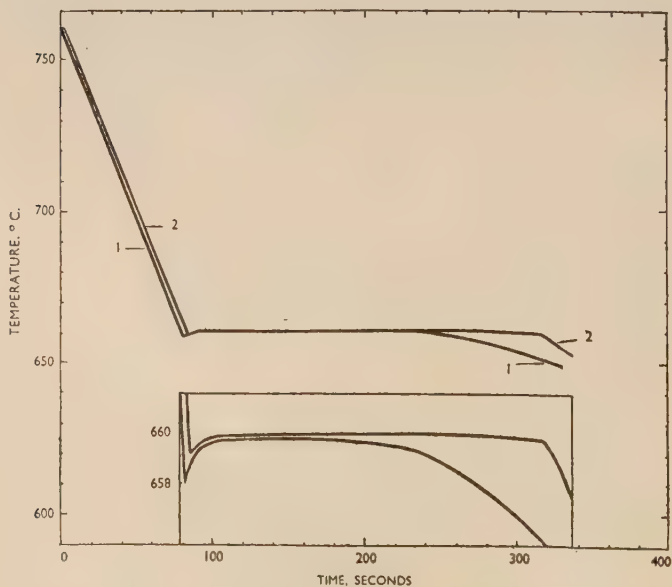


FIG. 11.—Slow Quiescent Solidification of Super-Pure Aluminium from 760° C.

Curve 1. Thermocouple $\frac{1}{8}$ in. from surface of specimen.
 „ 2. Thermocouple in centre of specimen.

Typical cooling curves obtained with air and water rates of cooling are shown in Figs. 9-11.

The results of quiescent cooling of super-pure and commercially pure aluminium over a range of cooling rates, obtained by quenching in water or oil, or by cooling in air or in the furnace, are summarized in Fig. 12. With super-pure aluminium the same degree of undercooling was found with all superheating temperatures ranging from 5° to 250° C. above the melting point. With commercially pure aluminium no undercooling could be observed if the temperature

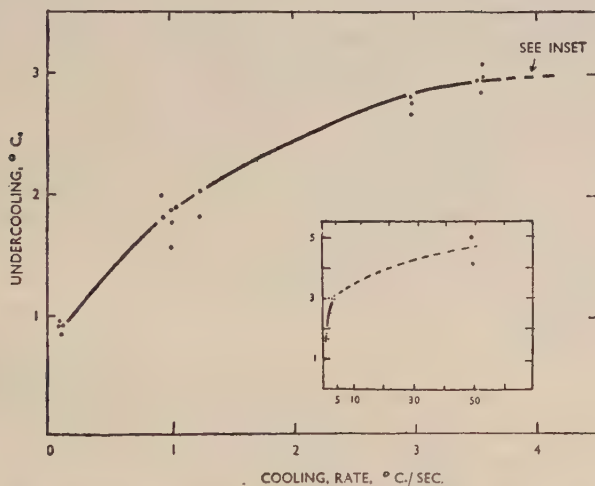


FIG. 12.—The Effect of Cooling Rate upon the Undercooling of Super-Pure Aluminium.

of superheating did not rise more than about 25° C. above the melting point. Above this temperature, the degree of undercooling of commercially pure aluminium was of the same order as that of super-pure aluminium.

When using the graphite crucible for several consecutive experiments, the degree of undercooling for a constant rate of cooling decreased with both metals. With an alumina crucible repeated melting had no effect.

IV.—DISCUSSION OF THE RESULTS.

Certain results obtained in this work are of considerable interest when considering the problem of nucleation of liquid metals. Perhaps

the most interesting question is that of residual nuclei remaining in melts at low temperatures of superheating of commercially pure aluminium.

With super-pure aluminium the number of grains in the cast structure appeared to be independent of the degree of superheating at all constant rates of cooling. No grain refinement was found even with charges that were just melted, with 1°–2° C. superheat, and immediately cast. It was not possible, therefore, to obtain any evidence, in the case of super-pure aluminium, in support of the residual kindred nuclei theory, as suggested for some other metals, e.g. bismuth.⁹ With commercially pure aluminium, on the other hand, a greater number of crystals (accompanied by different shapes of crystal at the same time) was obtained over a narrow range of superheating temperatures, 20°–25° C. approximately. The experiments summarized in Table I show that this phenomenon is reversible, since holding the metal for 30 min. at temperatures close to the liquidus, after superheating to 950° C., caused the finer cast structure to reappear. With shorter holding times after superheating, however, the coarse columnar structure was retained. It is also significant that no undercooling was observed when commercially pure aluminium was cooled from low superheating temperatures.

In an attempt to explain this behaviour, alloying elements were added consecutively to super-pure aluminium to make its composition approach that of commercially pure aluminium. Only when 0.02% titanium was added did these synthesized alloys give the same structure as the commercially pure aluminium after the same thermal treatment.

On the basis of this evidence, it appears that a titanium-containing constituent may remain undissolved in the liquid aluminium over a narrow temperature range above the melting point, and thus provide particles to act as foreign nuclei during subsequent solidification. The exact nature of this constituent, its changes with temperature, and the mode of its nucleating action were not studied.

The next most important factor which was observed to affect the cast structure of the two grades of aluminium was mechanical turbulence during the filling of the mould. Everything else being constant, the occurrence of turbulence on pouring leads to a greater number of grains in the cast structure. Furthermore, the purely columnar structure obtained with quiescent solidification changes into a columnar and centrally equi-axed structure with turbulent pouring of commercially pure aluminium (Table I). One explanation of the effects of turbulence is based on the assumption that during the filling of a mould the flowing liquid may carry nuclei particles (i.e. parts of solid crystals growing from the mould wall) from one part of the mould to another.⁸ An

additional and, in certain cases, an alternative explanation is suggested below, in considering the general problem of cast structures.

The third factor in order of magnitude of effect on cast structures is the rate of cooling. An increased rate of cooling (*a*) refines the columnar structure of pure metals, and (*b*) modifies the equi-axed structure of impure metals, first into a partly columnar and partly equi-axed structure, and secondly—at still higher rates of cooling—into a wholly columnar structure. Both of these effects have been well established in the past with numerous metals and alloys. An attempt was made in the present work to relate these changes to the thermal cooling cycle during solidification. The measurements of undercooling show that any grain refinement of a pure metal with increased rates of cooling is accompanied by an increased degree of undercooling. The formation of an equi-axed structure in the present work was found to be primarily due to the presence of alloying elements. These elements either provide constituents which act as foreign nuclei on solidification (such as are observed with commercially pure aluminium) or lead to solute concentration gradients during solidification (zone nucleation as observed by Northcott).¹⁰ When the effect of foreign nucleating particles is removed by using higher superheating temperatures, the effect of an increased rate of cooling on the structure of impure aluminium is analogous to the effects observed on super-pure aluminium. In the range of superheating temperatures over which the nucleating effect is still present in commercially pure aluminium, an increased rate of cooling partly suppresses the tendency to wholly equi-axed growth, and short columnar crystals are formed at the surface of the casting.

Grain refinement of pure metals with an increasing rate of cooling is consistent with the classical observation of Tammann¹ that the number of nuclei in the melt increases with an increasing degree of undercooling. According to the results now recorded, the degree of grain refinement obtained through small ranges of undercooling (e.g. 1°–5° C.) is of a smaller order of magnitude than the refinement obtained either through foreign nucleating agents or through mechanical turbulence.

In no case, in the present work, were fine “chilled” crystals observed at the surface of cast ingots. This particular phenomenon is being further investigated.

On the basis of the evidence available, the cast structures obtained with super-pure aluminium can be explained as follows: The time of the appearance of the kindred nuclei in the liquid is related to the rate of cooling. This time decreases rapidly with the degree of undercooling, as shown by Lange,¹¹ Scheil,¹² and Bardenheuer and Bleckmann.¹³

The faster the rate of cooling the more the liquid metal undercools,

since less time is allowed for the kindred nucleation to take place. The degree of undercooling is, in addition, controlled by experimental variables, e.g. crucible material, so that most of the data on undercooling cannot be used for a more rigorous thermodynamic analysis.

The first nuclei to appear, at finite rates of cooling, are at the mould surface. A nucleus (whose favourable direction of growth is in the direction of the temperature gradient, e.g. the [100] direction for copper) grows very rapidly along the mould wall, since the temperature is lowest in this region, until it meets a similarly growing crystal which has a different orientation. Each individual crystal then grows inward in the direction of the temperature gradient, the speed of growth being determined by the rate of cooling. The mode of growth of such columnar crystals has been explained by Northcott.¹⁴ Each columnar crystal consists of numerous cruciform branches of almost identical orientation which grow in the direction of the temperature gradient. This type of columnar growth has been confirmed in the present work by pouring out the residual liquid from partly solidified ingots and examining the growing crystal surfaces.

It is difficult to decide on the basis of the evidence available whether the number of nuclei which appear at any undercooling temperature, is the same as the number of columnar crystals finally observed in the cast ingots, or whether any nuclei having unfavourable growth orientations are swallowed by the favourably growing crystals.

With an increasing undercooling temperature the probability of the appearance of nuclei also increases, thus accounting for the finer grain-sizes observed. While such a thermodynamic explanation of nucleation in relation to the degree of undercooling is sufficient to account for the results obtained under the quiescent solidification, it provides little help in the explanation of the mechanical effects.

Two types of mechanical disturbance may occur during solidification: either the liquid is still flowing during the nucleation stage, or the liquid, though essentially static, is subject to vibrations of various frequencies. Either of these effects is known to lead to grain refinement.^{7,8} Under the experimental conditions used in the present work, it is suggested that the second type of mechanical effect may have been responsible for the observed grain refinement. As a result, the temperature distribution in the metal during the solidification stage, and hence the solute concentration gradients, are profoundly affected.

The full explanation of grain refinement with undercooling as well as with turbulence, requires further data about the structural changes in liquid metals on approaching the solidification temperature. Such data are also required to provide a satisfactory theory for the nucleation

effects of foreign nuclei. This theory is at present largely of a qualitative nature.^{2,3}

V.—CONCLUSIONS.

The main conclusion arising from the present work is that cast structures of pure metals, produced under controlled experimental conditions, can be correlated with the thermal history of the metal. The introduction of factors other than those of temperature (e.g. mechanical disturbances) or particles which may act as foreign nuclei, may completely outweigh the thermal factor in controlling the nucleation during solidification and hence in determining the cast structure.

ACKNOWLEDGEMENTS.

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SHEARING OF METAL BARS.*

1273

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SYNOPSIS.

Stresses, metal flow, and crack propagation in the shearing of $\frac{1}{2}$ in.-thick bars of most industrial metals, have been studied. It is found that there are two chief modes of fracture in shearing without clearance. Ductile materials undergo a bodily sliding action along the line of shear with the displaced particles maintaining their adhesion until final separation at full punch penetration. Other materials develop cracks, and the separation of the metal occurs either when one of the cracks propagates itself through the whole thickness of the bar or when the cracks from the punch and die meet; tongues of metal develop in the former case, while a clean fracture results from the latter.

Clearances up to 30% of the metal thickness were investigated, and optimum clearances for a clean fracture and least strain work are found to range from zero for ductile materials such as lead, tin, and aluminium, to between 5 and 10% for the harder metals such as copper, brass, and mild steel.

The effects of dullness of cutting edge and of tensile overstrain have also been assessed. These two factors tend to increase the maximum shearing load; but, whereas dullness increases the punch penetration at failure, overstrain tends to reduce it.

Finally, an attempt has been made to correlate the stresses in shearing and tensile tests, but there seems to be no definite and useful relationship between these two tests.

I.—INTRODUCTION.

HAVING regard to the large forces involved in the operation of sheet-metal blanking, and to the fact that these forces are commonly required at or near mid-stroke of a power press, where the crankshaft is in its weakest position, it is important that reliable information should be available concerning the actual forces and the strain work involved, the mechanism of fracture, and the effects of such factors as clearance and tool shear.

In order to provide data of value to sheet-metal users, tests have been undertaken on the blanking of sheet metals within the range of thicknesses commonly met with in industry, but a clearer conception of the actual behaviour of metal in the shearing operation is more likely to be obtained by following the development of fracture in a bar of substantial depth. With such a bar, it is possible to interrupt the shearing

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operation at various stages, to measure local strains in a way which would be quite impracticable with thin sheets, and to control such factors as clearance and sharpness more closely in proportion to the general dimensions of the specimen.

II.—PREVIOUS WORK ON BAR SHEARING.

A survey of existing literature on shearing reveals only a few papers of importance. In 1906, Izod ¹ conducted shearing experiments on a wide range of construction materials with a specially designed apparatus that enabled him to approximate closely the conditions of pure shear. He found that the ratio between the shearing and tensile strengths varied from 0.51 for Delta metal to 1.51 for cast iron. He also noticed a peculiar "knife-edge" left attached to the sheared surface of mild steel, and he attributed this to the obliquity of the cracks at their early stages of formation with the subsequent compression of the metal intervening between them. Goodman mentioned in the discussion on this paper that he had tried to correlate the shearing and tensile stresses in three different ways by comparing the nominal ultimate shearing stress with (1) the nominal ultimate tensile stress, (2) the true tensile stress at rupture, and (3) the shear stress found on a plane at 45° taken through the stricture of the broken tensile test bar, but that in all three cases he had found wide variations.

Regarding the shearing of mild steel, Crane ² found that with sufficient clearance, cracks from the cutting edges of the punch and die met, giving a clean break and a minimum power requirement, and that hard stock did not require nearly as much clearance for a clean fracture as soft stock. He also remarked that if the edges of the punch and die were dull, the punch must penetrate further to cause fracture, the peak load would be raised, and so greater power would be required to shear the specimen through.

In a more recent paper, Cook and Richards ³ investigated the variation of tensile/shear stress ratios in H.C. copper and 70 : 30 brass with different reductions by rolling. They found that these ratios diminished in value with increasing degree of cold working from 0.74 for annealed copper strip to 0.52 for fully hard strip, and from 0.77 to 0.52 for brass. Nominal and true tensile stresses were employed in the comparison, but only the nominal ultimate shearing stress. There is, in fact, an appreciable reduction in the shearing area before the maximum shearing load is reached, and this was not taken into account.

Other papers on blanking and punching are included in the references. ⁴⁻⁸

III.—EXPERIMENTAL.

1. *Description of Apparatus.*

The apparatus was designed to test rectangular bar specimens in double shear, the shearing taking place in sections sufficiently far apart to avoid any danger of interference in the shearing action at the two sections.

The apparatus is shown in Fig. 1. The specimen *T* is $\frac{1}{2}$ in. deep \times 1.5 in. wide \times 12 in. long and is sheared at two sections, 5 in. apart.

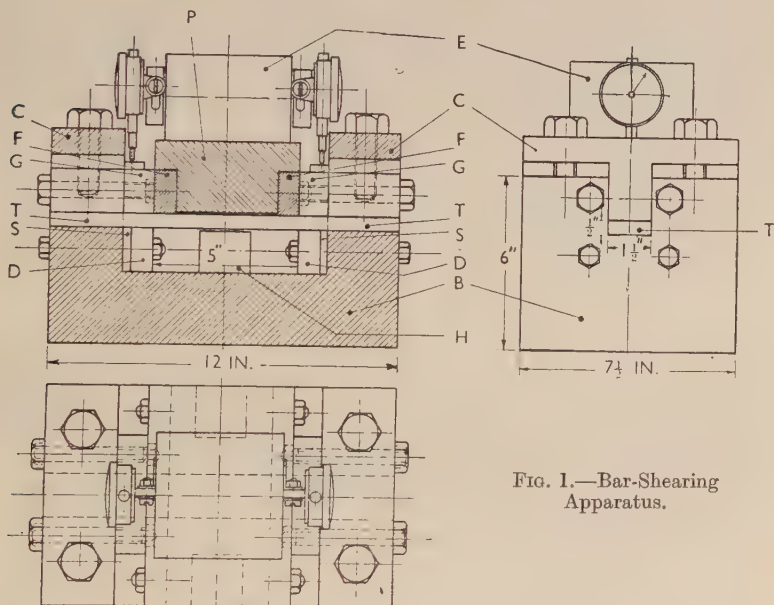


FIG. 1.—Bar-Shearing Apparatus.

It fits into a central slot, 1.5 in. wide, in the main body *B*; this prevents any tilting or lateral movement of the specimen but allows it some freedom to move longitudinally during the shearing operation. The die blocks *D* are securely bolted to the main body *B* through spacers *S*, which determine the distance between the two pairs of cutting edges and hence the effective clearance between the punch and die. For the earlier tests, the spacers were accurately ground so that there was no clearance, but later, sets of spacers were made, giving clearances up to 30% of the thickness of the bar. The punch *P* has two inserts *F* which form the actual cutting edges, and is guided by two blocks *G* bolted to the inside of the wings of the main body. The block *E* on top of the

punch serves to transmit the shearing load and at the same time acts as an attachment for the two 0.001 in. dial gauges, which are used to measure the penetration at each shearing edge of the punch. Two further blocks *H* are provided to prevent the punch from falling on to the heads of the bolts securing the die blocks *D* at the completion of a test. With the exception of the die blocks *D* and the punch inserts *F*, which are made of hardened die steel, the apparatus is constructed of mild steel. The robust construction of the apparatus proved sufficiently rigid to prevent any appreciable distortion under test.

2. Materials Tested and Preparation of Specimens.

The materials used in the present series of tests are enumerated in Table I, together with their mechanical properties. It will be noted

TABLE I.—*Mechanical Properties of Test Specimens.*

Material	Diamond Pyramid Hard- ness Number	Reduction in Area, % (Tensile)		Nominal Ultimate Stresses, tons/in. ²			Effective Stresses at Max. Load, tons/in. ²		
		At Max. Load	At Rupture	Tensile (<i>t</i> ₀)	Shear- ing (<i>s</i> ₀)	Ratio <i>s</i> ₀ / <i>t</i> ₀	Tensile (<i>t</i>)	Shear- ing (<i>s</i>)	Ratio <i>s</i> / <i>t</i>
Lead . . .	4.2	17	99	0.68	0.62	0.91	0.82	0.67	0.82
Tin . . .	6.0	23	92	0.99	0.80	0.81	1.30	0.99	0.76
Aluminium (1)	24.8	34	90	4.90	3.70	0.76	7.40	5.60	0.76
Aluminium (2)	28.2	39	81	4.70	4.20	0.89	7.80	6.20	0.79
Copper (1) .	81.2	24	65	15.20	10.00	0.66	19.50	12.70	0.65
Copper (2) .	93.3	2	63	18.70	11.60	0.62	19.20	13.90	0.72
Brass . . .	110.0	43	78	20.70	14.60	0.71	36.00	22.40	0.62
Mild steel (1) *	137.0	19	68	26.50	19.30	0.73	32.50	24.00	0.74
Mild steel (2) †	144.0	21	65	28.30	20.30	0.72	35.80	25.10	0.70

* Yield point 18.7 tons/in.²

† Yield point 17.5 tons/in.²

that two different stocks of mild steel, of copper, and of aluminium, differing somewhat in mechanical properties, were used. Their chemical compositions and some other physical and metallurgical characteristics are shown in Table II.

In order to study the development of strains in the specimen under the shearing operation, fine lines, 0.050 in. apart, were scribed on the faces of the bar for 0.5 in. on either side of the shearing section. These lines were scribed in a milling machine by means of razor blades, so as to ensure precision and avoid interference with the development of

TABLE II.—*Chemical Composition and Initial Dimensions of Test Specimens.*

Material	Source of Specimen	Grain-Size, mm.	Chemical Composition
Lead . . .	Specimen $0.483 \times 1.475 \times 12$ in.; produced by extrusion	...	Pb 99.991, Cu 0.0045, Ag 0.0045%
Tin . . .	Cast bars subjected to 40% reduction by rolling before shear test	...	Chempur
Aluminium (1)	Rolled sheet; fully annealed	...	Al 99.546, Fe 0.30, Si 0.14, Cu 0.005, Mn 0.006, Zn 0.003%
Aluminium (2)	Extruded rod	...	Al 99.308, Fe 0.38, Si 0.27, Cu 0.015, Mn 0.020, Zn 0.007%
Copper (1) .	Rolled bar	0.065	Cu 99.93, Fe 0.005, Ni 0.01, Ag 0.005, O 0.05%
Copper (2) .	Specimen $0.490 \times 1.500 \times 12$ in.; rolled bar	0.04	Cu 99.95, Fe 0.005, Ni 0.01, Ag 0.005, O 0.03%
Brass . . .	Rolled bar	...	Cu 70, Zn 30%
Mild steel (1) *	Rolled plate	...	C 0.12, Mn 0.45, Si 0.07, S 0.026, P 0.023%
Mild steel (2) †	Rolled plate	...	C 0.18, Mn 0.57, Si 0.055, S 0.047, P 0.027%

* Sulphur prints showed uniform distribution of sulphides. Decarburization to a depth of 0.007–0.14 in.

† Sulphur prints showed small amount of central segregation. No decarburization.

strain and cracks. In a scribing operation of this kind, errors in the spacing and parallelism of the lines are inevitable. In every case, therefore, the spacing of the scribed lines was checked by means of a travelling microscope reading to 0.0001 in.

3. Scope of Investigation.

The experimental work can be divided into three main parts. The first is concerned with plastic flow and crack propagation in the shearing process with tools of no clearance; the second deals mainly with the effects of clearance, and the third with miscellaneous effects such as dullness of cutting edges.

In setting the specimen in the testing machine care was taken to ensure that the centres of the transversely scribed areas were exactly

in the planes of the cutting edges of the punch and die. No special precautions were taken to ensure axial loading of the punch; the whole apparatus was centred by eye on the moving crosshead of a 100-ton Armstrong-Whitworth hydraulic testing machine. Any seriously non-axial loading would, of course, result in the punch jamming between the guide blocks, but any difference in the amount of penetration at the two shearing edges of the punch would soon be noticed from the dial-gauge readings and the operation could be stopped before any damage resulted. No difficulties of this kind were, in fact, encountered.

Only two quantities were actually measured during a test: the shearing load, by means of the pressure gauge on the testing machine, and the punch penetration, by means of dial gauges.

The first specimen of each metal was sheared right through to obtain a complete load/penetration curve. In order to study the development of strains and the progress of fracture, several specimens from each metal were subjected to partial shearing tests with zero clearance: one specimen was sheared to the point of maximum load, while other bars were sheared to stages intermediate between the point of maximum load and complete fracture. In the cases of tin and lead, owing to shortage of material, only one bar was used. This was sheared successively to maximum load, an intermediate point, and complete rupture, and was removed at each stage for measurements. It was found in some cases, particularly with aluminium, that care was necessary to avoid distortion and damage in removing the bar from the apparatus. In certain cases, the fall of load after maximum was so rapid that no partial testing was possible beyond this point. Where such tests were possible, the load/penetration diagrams from the partially- and completely-sheared tests were found to be mutually consistent except in the case of mild steel, where the rate of crack propagation and fracture appeared to vary with different specimens. Typical load/penetration curves from these tests will be found in Fig. 2.

In order to determine the distribution of strains after partial or complete shearing, it was necessary to make careful measurements of the network of scribed lines. In the first instance, measurements of the strained network were made by means of the travelling microscope. This method involved the taking of many observations and much labour in plotting. In fact, in the earlier tests, over 5000 separate observations had to be made on each specimen after straining. It was found, however, that there was, within the limits of measurement, perfect agreement between each set of four traced networks, and that there was insignificant distortion in the networks on the upper and

lower faces. It was therefore decided that with later specimens it would only be necessary to scribe a single network of lines on one edge to obtain an accurate and representative distribution of strain.

Further to reduce the labour of measurement, an attempt was made to project the scribed network by means of an epidiascope and to trace the enlarged image on tracing paper. This method had the advantage that the whole network could be projected and traced at one setting of the specimen in the epidiascope. It was found, however, that the greatest magnification that would afford the necessary definition (10 times) was insufficient to give the necessary precision, that a greater magnification led to dispersion and consequently no improvement in accuracy, and that the depth of focus of the epidiascope was insufficient to provide a clear image in regions of very severe plastic strain. In the interests of accuracy it was therefore decided to make complete measurements of one scribed network on the edge of the specimen. Typical results of these measurements will be found in Figs. 3 and 4.

The method of introducing clearances between the tools has already been described. These clearances were always checked by feelers and standard gauge blocks before testing.

In order to investigate the effect of dullness of cutting edge, a special jig was designed and constructed, by means of which it was possible to grind any predetermined radius on the cutting edges of the punch and die blocks. In fact, three radii of 0.005, 0.010, and 0.020 in. were produced and these were applied only to mild steel and aluminium specimens.

IV.—DISCUSSION OF RESULTS.

1. *Using No Clearance.*

(a) *Load/Penetration Curves.*

From the curves shown in Fig. 2 it will be seen that the shearing load for all metals tested reaches a maximum value after the punch has penetrated some 10–37% of the specimen, and that from this point onwards the load falls away, reaching zero when fracture is complete.

It is found, however, that the characteristic shape of the load/penetration curve varies not only with different metals but also with different stocks of the same metal. The curves for lead, tin, and aluminium are very similar and are characterized by a gradual rise to the point of maximum load and an equally gradual fall from it. The curves for the two stocks of copper are similar on the whole, but the initial rise in the curve of copper (2) is much more rapid than that of copper (1). Although the main resistance to shearing falls away at about 80% pene-

tration in both coppers, they offer a substantial frictional resistance up to the point of full penetration. In the case of brass, the bending-

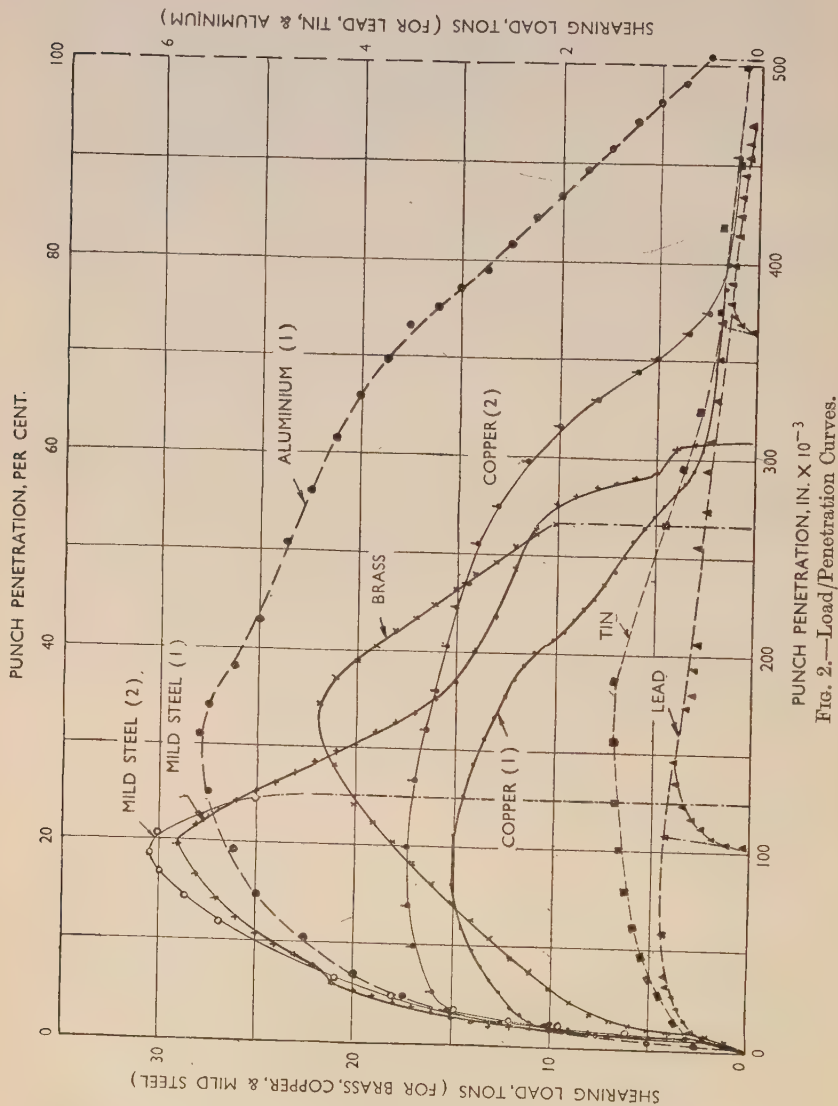


Fig. 2.—Load/Penetration Curves.

over of the curve occurs quite early, but the maximum load is not reached until the punch has penetrated about 37%. After that,

the fall in load is rapid and the bar is separated at about 53% penetration. The two stocks of mild steel both rise sharply to the maximum and fall rapidly, and fracture is complete when the punch has penetrated 25% in mild steel (2) and 60% in mild steel (1).

(b) *Mechanism of Fracture.*

A summary of results of tests with no clearance will be found in Table III; while strained networks of scribed lines show the progression of fracture in different metals (Figs. 3 and 4).

TABLE III.—*Shear-Test Results* (Clearance : Nil).

Material	No. of Test-Piece	Max. Shearing Load, tons	Nominal Ultimate Shearing Strength, tons/in. ²	Punch Penetration, %		Effective Shearing Stress at Max. Load, tons/in. ²
				At Max. Load	At Complete Failure	
Lead	0.88	0.62	12	100	0.67 *
Tin	1.21	0.80	19	100	1.00 *
Aluminium (1)	a	5.7	3.8	35	...	5.9
„	b	5.4	3.6	35	...	5.6
„	c	5.5	3.7	34	100	5.6
Aluminium (2)	a	6.5	4.3	30	...	6.2
„	b	6.2	4.1	29	...	5.8
„	c	6.5	4.3	31	95	6.3
Copper (1) .	a	15.2	10.1	21	...	12.8
„ .	b	15.2	10.1	18	...	12.3
„ .	c	15.1	10.1	21	78	12.6
Copper (2) .	a	17.3	11.5	16	...	13.8
„ .	b	17.3	11.5	15	...	13.6
„ .	c	17.4	11.6	14	...	13.5
„ .	d	17.5	11.6	21	80	14.6
Brass . .	a	22.1	14.7	36	...	22.8
„ . .	b	21.2	14.1	36	...	21.9
„ . .	c	21.0	14.0	37	53	22.1
Mild steel (1) .	a	29.4	19.6	20	...	24.5
„ .	b	29.0	19.3	18	...	23.7
„ .	c	28.9	19.3	20	...	23.8
„ .	d	29.0	19.3	19	62	24.1
Mild steel (2)	30.4	20.3	19	25	25.1 *

* Values from single fractured specimen only.

Referring to the network diagrams for lead in Fig. 3 (a) and (b), it will be seen that the distortion is local and regular and that there are no signs of cracking at any stage. It will be noticed from the figure that there are evidences of bodily shear revealed by the discontinuity of some of the longitudinally scribed lines. There seems little doubt that with lead and tin, bodily shearing can occur without

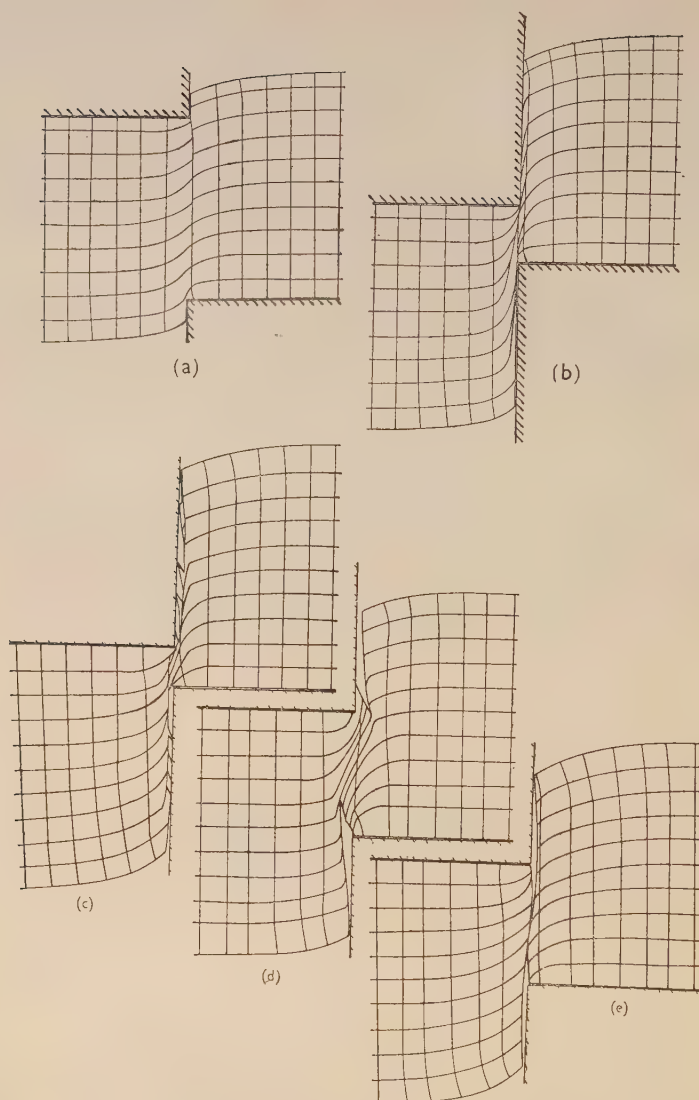


FIG. 3 (a)–(e).—Network Diagrams Showing Progression of Fracture in Shearing Metal Bars. (Clearance : nil.)

(a) Lead; 22% penetration.

(b) Lead; 74% penetration.

(c) Aluminium (1); 86% penetration.

(d) Copper (1); 55% penetration.

(e) Brass; 53% penetration.

separation, or at least with immediate re-attachment. The ultimate severance of the lead bar occurred, as with tin, at 100% penetration, when the tool edges met. The sheared surface was extremely clean and smooth. The shearing process with this fine-grained sample of pure lead may be regarded as a "copy-book" standard of pure plastic shearing and as a basis for comparison with other metals. Tin behaves in much the same way as lead and therefore requires no further description.

A process very similar to that described above occurred in the shearing of aluminium (1). In this case abortive cracks formed at the edges which are shown clearly in Fig. 3 (c), but these were evanescent and did not penetrate far into the bar. With aluminium (2), however, large cracks extending right across the width of the bar formed in addition to the abortive cracks at the edges. As a result, tongues of metal were left behind to disfigure the sheared surface, in contrast to the clean and smooth sheared surface of aluminium (1).

This difference in behaviour of the two samples of aluminium under shear was at first thought to be due to the mechanical treatments they had received before shearing; aluminium (1) was obtained from a rolled plate, while aluminium (2) was from an extruded rod. Major P. C. Varley of The British Aluminium Company, Ltd., who conducted a chemical analysis of the two stocks, was, however, of the opinion that this difference in previous mechanical working was not likely to affect their behaviour in shearing. He provided test results to demonstrate that the shear strength of aluminium is very sensitive to impurities, so that the variation in the purity of the two stocks (99.31% for aluminium (2) as against 99.55% for aluminium (1)) might have accounted for differences in the shearing process.

Like aluminium, the two stocks of copper also showed marked difference in their process of fracturing under shear. Whereas copper (2) behaved in a very similar way to the basic plastic materials, with the formation only of abortive cracks at the edges, prominent crack formation and propagation occurred with copper (1), as shown in the network diagram in Fig. 3 (d).

This difference in behaviour under shear could not be attributed to their composition, which was practically the same for the two stocks (see Table II). Dr. Maurice Cook of Imperial Chemical Industries, Ltd., who conducted the chemical analysis, pointed out, however, that the physical properties of the two stocks were not the same; neither stock was in the fully-soft condition for which the D.P. hardness number should be about 55, and the difference in hardness and grain-size might account for the difference in behaviour on shearing.

In the shearing of brass, a single crack formed at an early stage, ahead of the edge of each tool. This crack propagated itself very rapidly, and although the cracks from the punch and die showed a tendency to start obliquely, they soon turned towards each other and complete rupture occurred at the relatively early stage of 55% penetration. There was no sign of a tongue, even at the edges, and the surface of rupture was quite clean (Fig. 3 (e)).

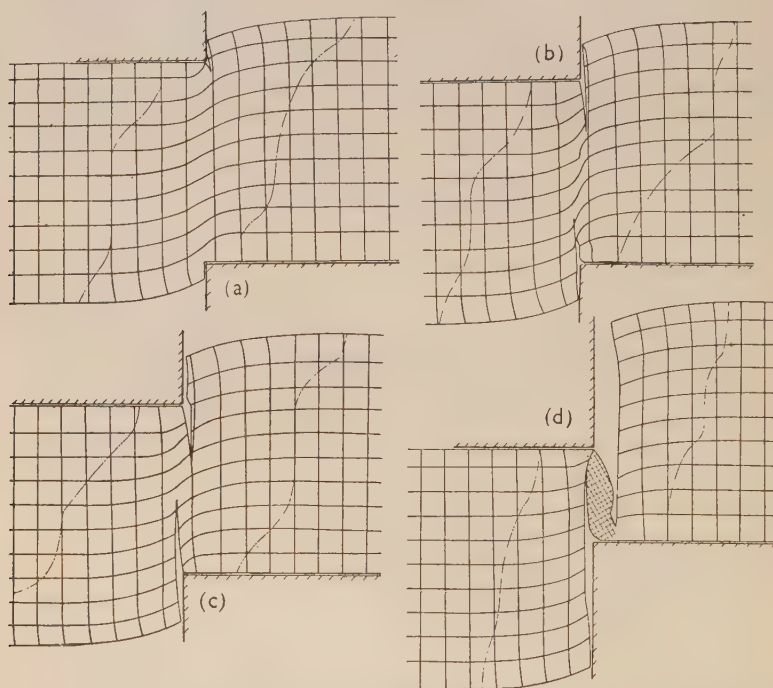


FIG. 4.—Network Diagrams Showing Progression of Fracture in Shearing of Mild Steel (1). (a) At maximum load; (b) 25% penetration; (c) 32% penetration; (d) 60% penetration. (Clearance : nil.)

The behaviour of the two stocks of mild steel under shear varied considerably. Mr. W. E. Bardgett of the United Steel Companies, Ltd., undertook a comparative examination and reported the results shown in Table II. He suggested that the differences in behaviour might be attributable to the decarburized surface of mild steel (1) and also to its lower carbon and manganese contents, resulting in a somewhat lower hardness.

The progress of fracture in mild steel (1) is shown in Fig. 4. At

maximum load (Fig. 4 (a)) there were already visible signs of crack formation at one of the shearing edges. By the time the penetration had reached 25% (Fig. 4 (b)), cracks had penetrated a considerable distance beyond the shearing edges, and the subsequent progress of the cracks is shown in Fig. 4 (c) (32%) and Fig. 4 (d) (60% penetration and imminent separation). It will be noticed that the two cracks, which appeared to be substantially tensile in character, tended to develop in parallel directions but not exactly parallel to the shearing faces of the punch and die. Consequently a tongue of metal was left behind between these cracks, which at the following stage (c) was being compressed between the advancing faces of the tool until it took the highly distorted form shown shaded in Fig. 4 (d). The tongue eventually became burnished as the punch or die-face passed over it, and this could be clearly seen on the fractured section. The compression of the tongue induced a force tending to separate the two sections of the bar under shear. Figs. 4 (b), (c), and (d) show that this separation developed to a marked extent if either part of the bar was relatively free for longitudinal displacement.

Whereas in mild steel (1) the two cracks from the punch and die continued to develop along separate lines leading to the formation of the tongue, delaying the rupture, and increasing the strain work, in mild steel (2) the cracks, after just overlapping, suddenly converged and met, causing immediate rupture, leaving no more than a vestigial tongue, and eliminating the strain work due to the compression of the tongue.

As a matter of interest, chain-lines have been inserted in Fig. 4 to indicate the region over which the maximum linear shear exceeds 2% in each case. Similar lines will be found in Figs. 5, 6, and 7.

From the difference in behaviour in the shearing of the two stocks in the cases of aluminium, copper, and mild steel, it seems clear that the propensity for crack propagation, which largely controls the process of shearing, is very sensitive to some property of the material which varies in the two stocks.

Two possible measures of ductility in the tensile test are: (a) reduction of area at maximum load (corresponding to general elongation), and (b) ultimate reduction at fracture. Remembering that crack propagation is more rapid in aluminium (2), copper (1), and mild steel (2), reference to Table I, columns 3 and 4, shows that neither of these reductions correlates satisfactorily in all cases. The ultimate reductions might however correlate if allowance could be made for the initial work-hardening of copper (2), which is revealed by the figures for reduction at maximum load in column 3.

2. Effects of Clearance.

The numerical data from tests with different clearances will be found in Table IV; while the strained networks of lead, copper, and mild

TABLE IV.—*Shear Test Results with Various Clearances.*

Material	Clearance, %	Max. Shearing Load, tons	Ultimate Shearing Strength, tons/in. ²	Punch Penetration, %		Work Done, in.-tons
				At Max. Load	At Complete Rupture	
Lead . . .	nil	0.88 *	0.62 *	12 *	100 *	0.25 *
" . . .	10	0.95 *	0.67 *	17 *	90 *	0.36 *
" . . .	20	0.84 *	0.59 *	18 *	104 *	0.33 *
" . . .	30	0.81 *	0.57 *	19 *	124 *	0.40 *
Tin . . .	nil	1.21 *	0.80 *	19 *	100 *	0.34 *
" . . .	10	1.23 *	0.82 *	27 *	84 *	0.37 *
" . . .	20	1.18 *	0.79 *	30 *	109 *	0.48 *
" . . .	30	1.07 *	0.71 *	56 *	142 *	0.53 *
Aluminium (2)	nil	6.4	4.2	31	95 *	2.14 *
Aluminium (1)	nil	5.5	3.7	34	100 *	1.97 *
"	5	5.3	3.5	41	78 *	1.57 *
"	10	5.4	3.6	45	67 *	1.52 *
"	20	5.3	3.6	53	71 *	1.62 *
"	30	5.1	3.4	86	118 *	2.33 *
Copper (2) .	nil	17.4	11.6	21	80 *	5.38 *
Copper (1) .	nil	15.1	10.1	21	78 *	3.49 *
" . . .	5	15.0	10.0	23	76 *	2.82 *
" . . .	10	14.8	9.7	25	38 *	2.37 *
" . . .	20	14.7	9.6	35	39 *	2.54 *
" . . .	30	14.7	9.7	46	53 *	3.46 *
Brass . . .	nil	21.0	14.0	37	53 *	4.22 *
" . . .	5	20.9	13.9	38	43 *	3.28 *
" . . .	10	20.7	13.8	40	46 *	3.43 *
" . . .	20	20.3	13.6	48	52 *	3.94 *
" . . .	30	19.9	13.3	59	76 *	5.69 *
Mild steel (1) .	nil	29.1	19.4	19	62 *	5.48 *
Mild steel (2) .	nil	30.4 *	20.3 *	19 *	25 *	2.90 *
" . . .	5	30.2	20.1	21	22 *	2.50 *
" . . .	10	30.0	20.0	23	28 *	3.27 *
" . . .	20	29.6	19.7	30	32 *	3.81 *
" . . .	30	29.0	19.4	35	43 *	5.00 *

Note.—The values given in the Table are the averages of three tests on separate specimens unless otherwise noted.

* Values from single fractured specimen only.

steel are shown in Figs. 5, 6, and 7, which also contain load/penetration curves for the different clearances.

It will be seen from Fig. 5 that in the case of lead, clearance permits

a greater initial bending and therefore more severe distortion near the line of tool action. As a result, the penetration at maximum load is

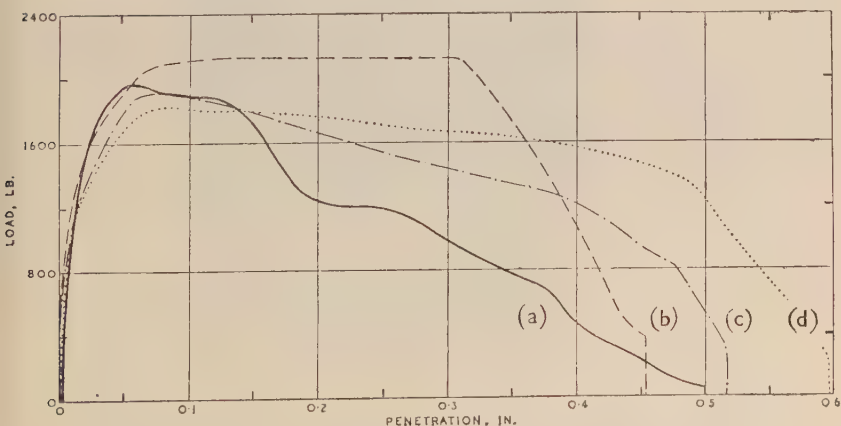
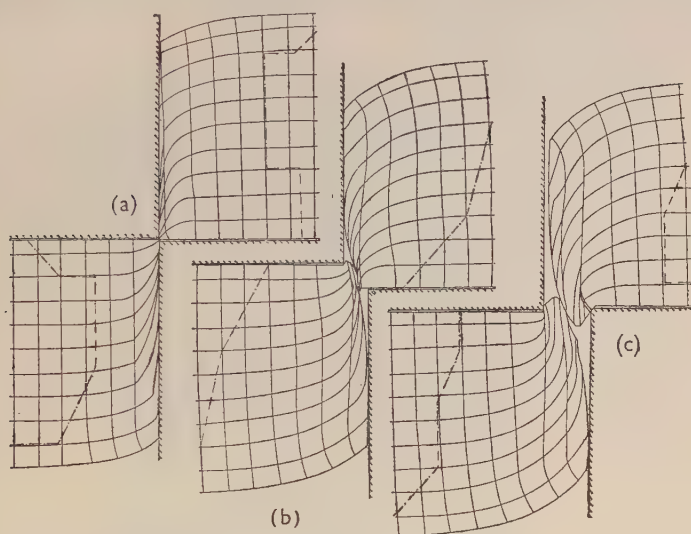


FIG. 5.—Effect of Clearance on Fracture in Shearing of Lead. (a) Nil; (b) 10%; (c) 20%; (d) 30%.

increased, the material in the clearance region comes under increasingly tensile conditions, and with the 20% clearance, the ultimate fracture appears largely tensile in character. The work required to complete the severing operation increases substantially with clearance as is shown

in Table IV. This is also no doubt associated with the fact that as the clearance is increased, more material takes part in the drastic distortion which precedes tensile rupture. The sustained high punch load for

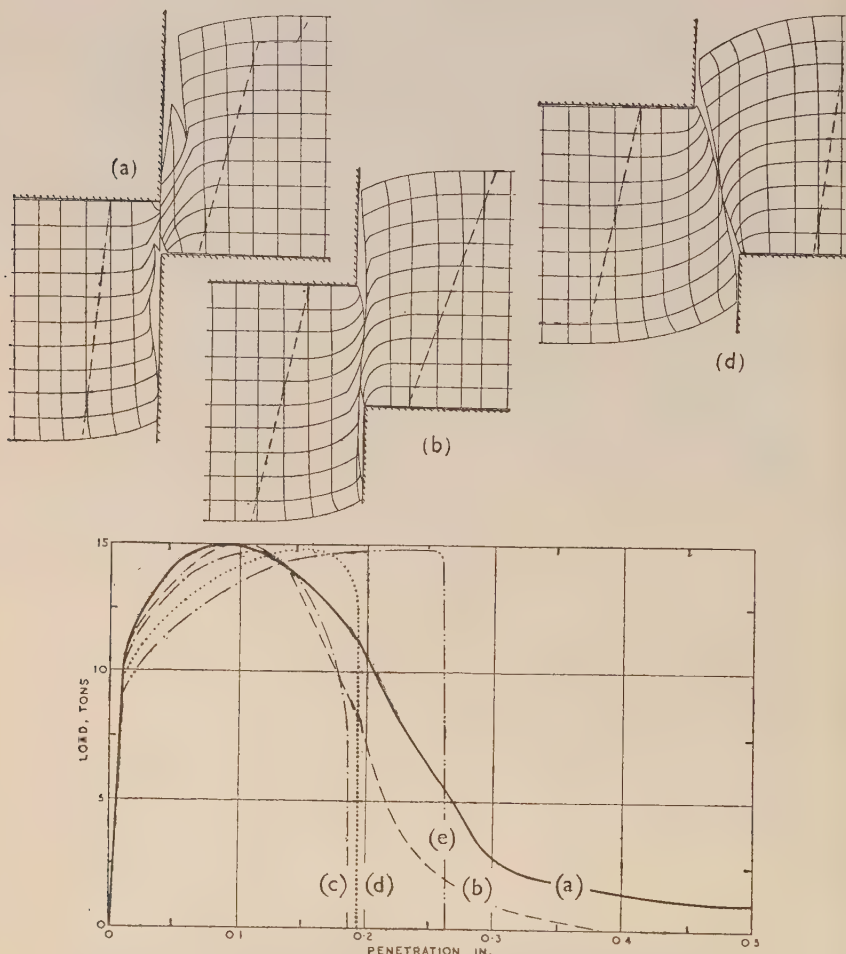


FIG. 6.—Effect of Clearance on Fracture in Shearing of Copper (1). (a) Nil; (b) 5%; (c) 10%; (d) 20%; (e) 30%.

lead at 10% clearance is not easy to explain, but there is no doubt that it occurred, since the methods of experiment and measurement were simple. Unfortunately, there was no spare bar with which to repeat the test.

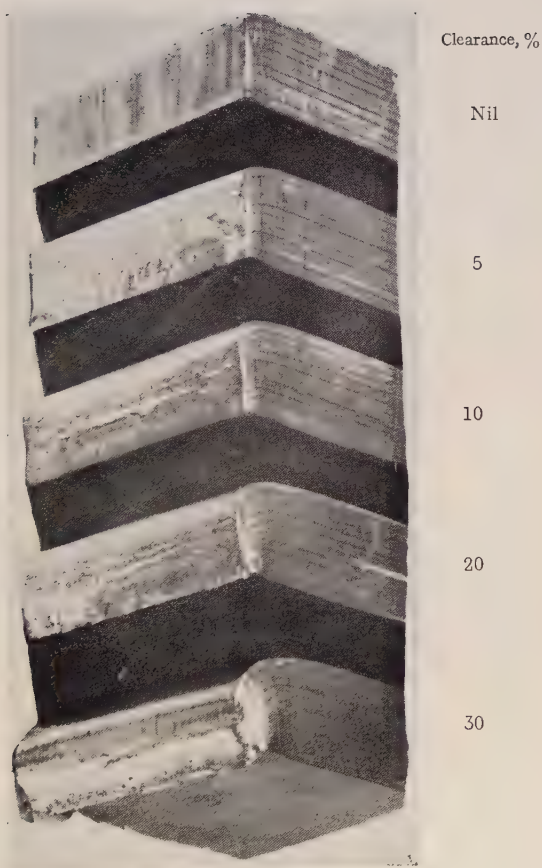
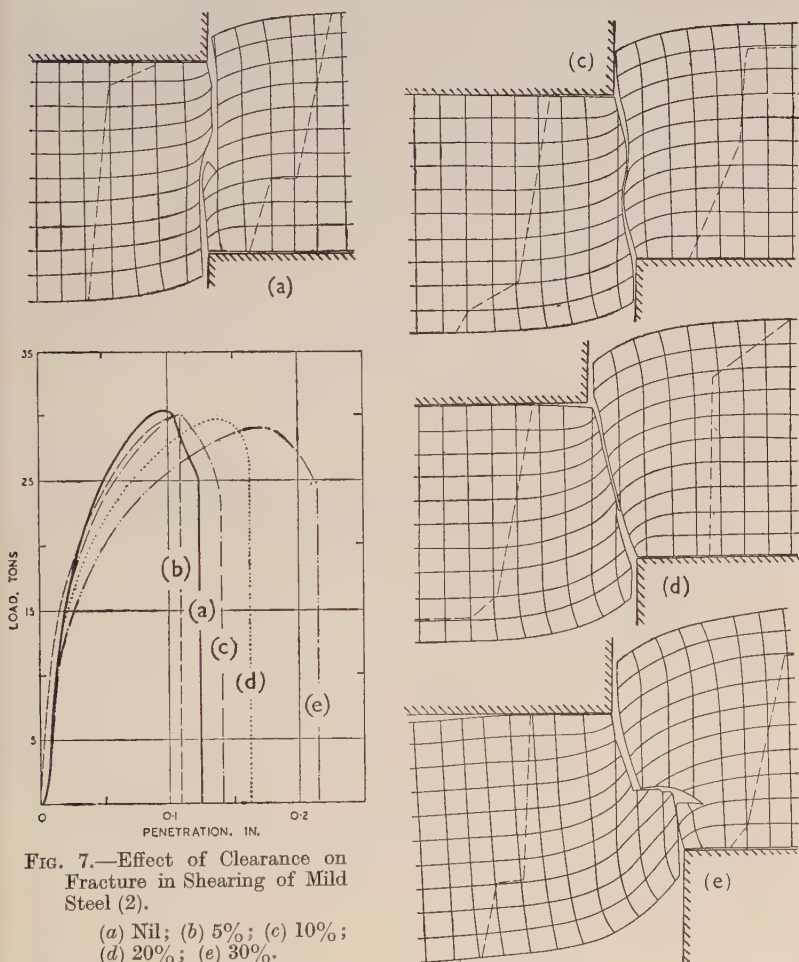


FIG. 8.—Appearances of Sheared Bars of Aluminium.

The behaviour of tin bars under different clearances is practically the same as that described above for lead. Hence, from every point of view—minimum work, clean surface, and least general distortion—the clearance to be recommended for both lead and tin is the smallest practicable.



The effect of clearance on the mode of rupture in aluminium bars follows the same trend as in lead and tin. Even when the clearance is as small as 5%, the clean shearing action is lost and cracks develop across

the full width of the bar. This trend is shown clearly by the series of photographs of sheared surfaces obtained with increasing clearance (Fig. 8, Plate XXVIII). It will be seen from Table IV that the work done in the shearing operation falls to a minimum at 10% clearance, but against this the severed surfaces are far less perfect than with zero clearance; and it seems obvious that with pure aluminium at least there is no justification for adopting any greater clearance than is necessary for practical purposes. The recommendation of 10–14% clearance for aluminium by some authorities ^{9, 10} appears surprisingly high in the light of the present results, but may prove to be necessary for metal containing more impurities.

Fig. 6 gives network diagrams for copper (1) with different clearances. It will be seen that 5% clearance eliminates the tongue and produces a much cleaner fracture. The fracture remains clean up to 30% clearance, but the strain work is a minimum at 10% (Table IV). The tests suggest that with copper similar to this there are clear advantages in adopting a clearance of 5–10%.

Clearance has comparatively little effect on the fracture of brass, which remains clean up to 20% clearance. However, there is a definite reduction in the strain work at 5%. With 30% clearance, the cracks at the punch and die start too far apart to converge, and one of them develops more rapidly than the other and continues right across the bar, causing ultimate rupture. It appears, therefore, that for rolled brass, any clearance between zero and 5% should produce satisfactory results.

Fig. 7 shows the effect of clearance on the shearing of mild steel (2). It is apparent that if an appropriate clearance is provided, the two cracks from the punch and die will meet, producing a relatively clean though oblique surface of fracture and eliminating the distortional work required to crush the inter-crack tongue. The cleanest surface, apart from any other consideration, is obtained with 20% clearance, but the surface at 10% is not much inferior and geometrically is, of course, more satisfactory. At 5% the convergence of the cracks is imperfect, but there are no signs of any significant tongue. At 30% clearance the cracks are united ultimately by a transverse rupture which appears largely tensile in character (Fig. 7 (e)) and which obviously has no practical recommendation.

To obtain an idea of the spread and the degree of straining of the mild steel bars at different clearances, hardness tests were carried out on the longitudinal section of the middle of the bar. The average of three tests, one at the upper surface, one at the lower surface, and one at the middle of the section, has been plotted in Fig. 9. It will be seen

that as the clearance is increased, there is a general increase in hardness at and near the shearing plane. Moreover, the zone of hardness-increase also widens with clearance; this is consistent with the load/penetration characteristics and the straining of the network of scribed lines.

Having regard to the various effects, it would appear that the optimum clearance for mild steel is in the range 5-10%, according as geometry or the surface condition is the leading consideration. In the former case it will be seen that the present series of tests endorses the almost unanimous recommendation of the various technical books that the appropriate clearance for soft steel is 5%.

3. Miscellaneous Effects.

(a) Dullness of Cutting Edges.

The results from tests are shown in Figs. 10 and 11 for mild steel and aluminium, respectively. It will be seen that the maximum shearing load, the punch penetration at maximum load, and the work done, all increase with increasing radius on the cutting edges.

The network diagrams of mild steel for the various radii show that a

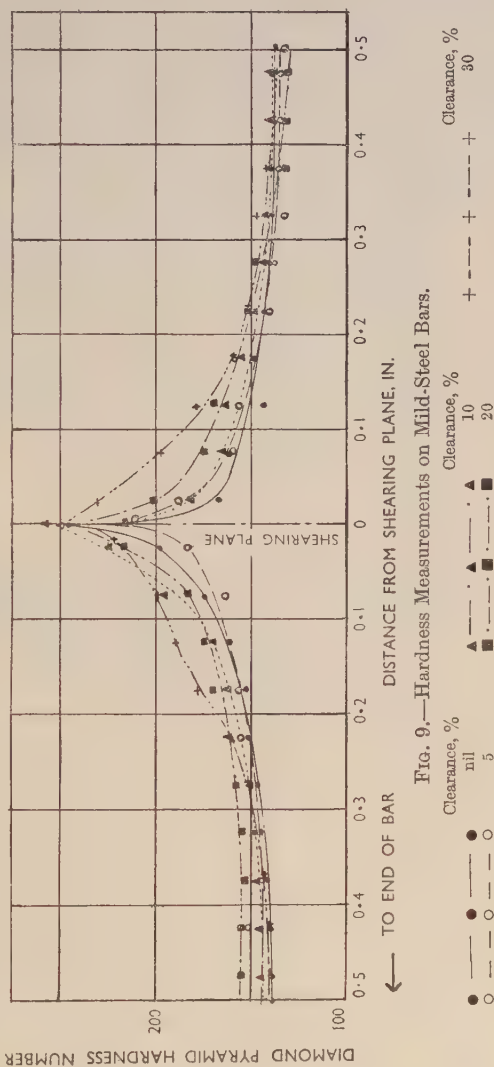


Fig. 9.—Hardness Measurements on Mild-Steel Bars.

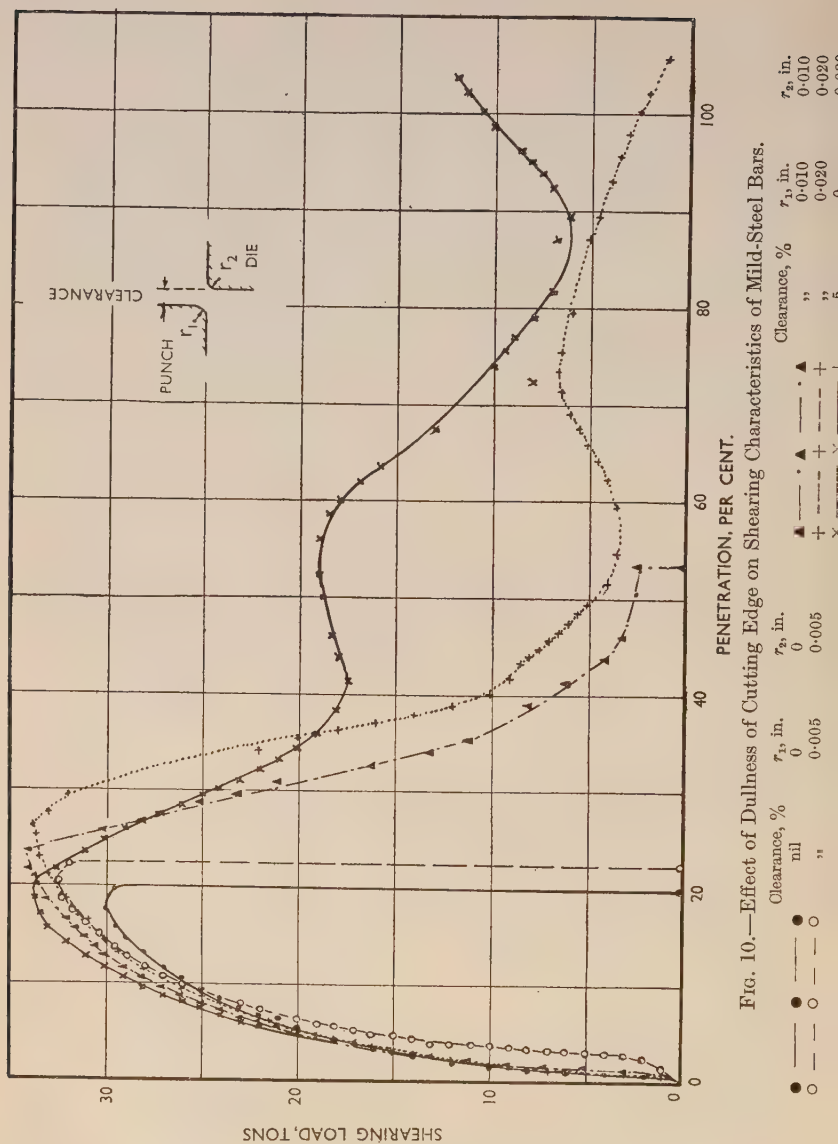


Fig. 10.—Effect of Dullness of Cutting Edge on Shearing Characteristics of Mild-Steel Bars.

0.005 in. radius has little effect on the geometry of the sheared edges, when compared with the sharp-edged tool. A radius of 0.010 in., however, produces marked differences; the size of the tongue is increased

substantially, and the end sheared section is displaced considerably away from the punch. With the 0.020 in. radius, a prominent tongue is left attached to the end (outer) section; while a smaller tongue, which has also been well burnished, remains attached to the middle sheared section.

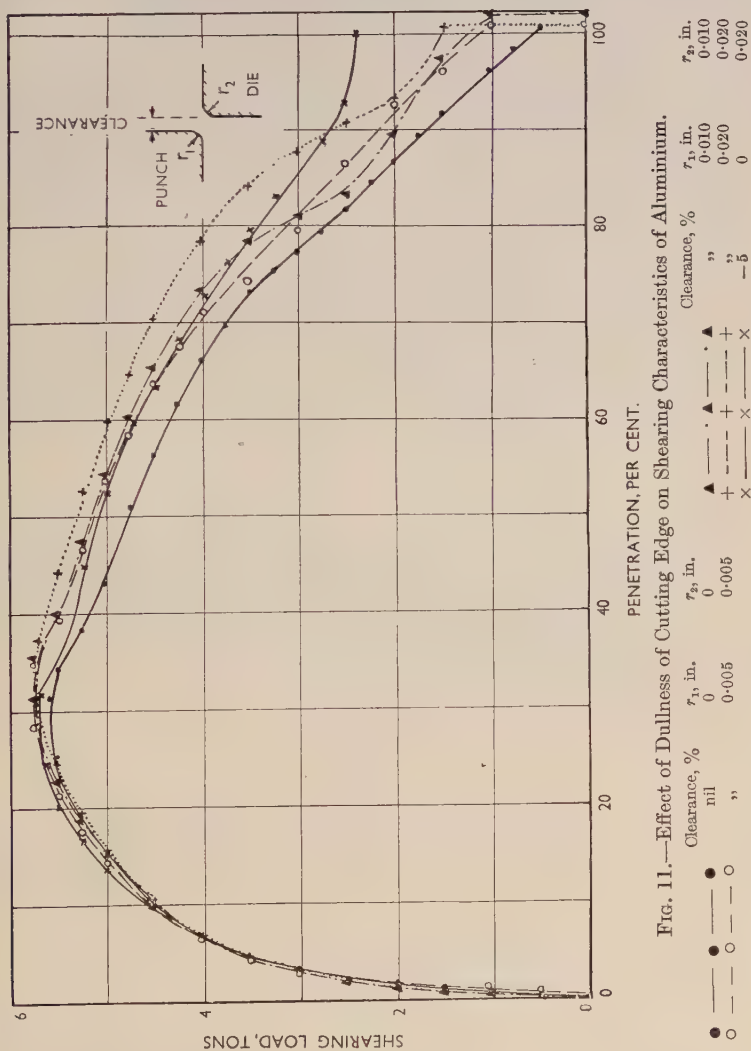


FIG. 11.—Effect of Dullness of Cutting Edge on Shearing Characteristics of Aluminium.

In the case of aluminium, all the sheared surfaces are clean and well burnished by tools of the various radii, while incipient cracks are present in all cases.

(b) *Negative Clearance.*

Negative clearance, in combination with the dulling of the cutting edge of the die, has been employed in industry to produce aluminium slugs, for the extrusion of collapsible tubes, that require highly polished edges.

In order to investigate the effect of this combination, a negative clearance of 5% was provided on the apparatus. The cutting edges of the punch were kept sharp, while a radius of 0.020 in. was put on the cutting edges of the die blocks. Mild steel and aluminium bars were tested under these conditions.

The load/penetration curves from these tests are included in Figs. 10 and 11. In the case of mild steel (Fig. 10) the sharp edge of the punch has clearly accelerated the initial crack formation (at 20% penetration), but the negative clearance has caused a substantial tongue to form between the developing cracks and so has checked the fall of the pressure curve between 40 and 70% penetration. Since, moreover, the sheared surfaces were very rough, it is clear that this tool arrangement is unsatisfactory for mild steel. On the other hand, with aluminium (Fig. 11), where fracture is more nearly by true shear, the shearing tendency, which is predominantly along the lines joining the cutting edges of punch and die, is oblique owing to the negative clearance, and so introduces an element of extrusion as the potentially tapered blank is forced through the restricted and rounded die aperture. This has the effect of (i) slightly increasing the punch load during the period of extrusion, and (ii) producing a highly burnished sheared surface. The use of negative clearance with a rounded die edge is therefore clearly justified in the case of aluminium.

(c) *Tensile Overstrain.*

In order to investigate the effect of previous tensile overstrain, brass and aluminium specimens were subjected to tensile pull until the middle lengths of 6 in. were elongated 10, 20, and 30%. These overstrained bars were machined down to the same dimensions as the 30% stretched bar (0.436×1.337 in.) and then used in the shearing test.

The stress/penetration curves from the tests on brass are shown in Fig. 12. It will be seen that there is a systematic rise in the nominal shearing strength and an advancement of the point where the curves begin to bend over. There is also a systematic reduction in the punch penetration at failure. For aluminium, however, these effects are not so evident.

There seems little difference in the appearance of the fractured

surfaces of the bars with different overstrains. Incipient cracks are present in all the aluminium bars and the sheared surfaces of brass all appear to be similar. Hence, it appears that the overstraining of these two metals by tension affects only the stress/penetration relationships and has very little effect on the process of fracture.

V.—STRESS/STRAIN RELATIONSHIPS.

To judge from existing literature on shearing, no attention seems to have been paid to the behaviour of the metal beyond the point of maximum load, and the shearing strength has been calculated by dividing the maximum load by the original area of the sheared section.

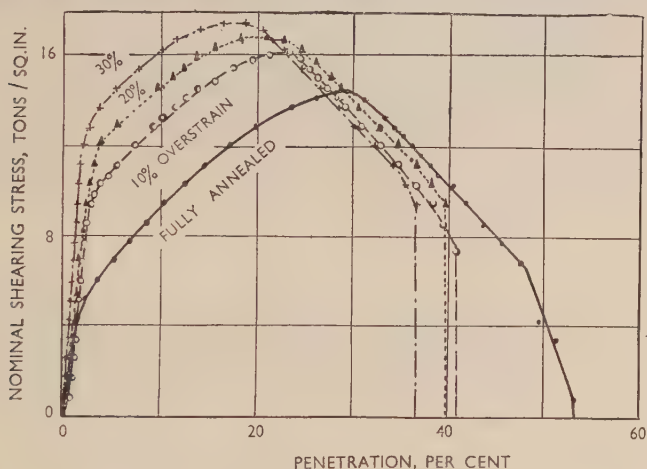


FIG. 12.—Effect of Tensile Overstrain on Shearing Characteristics of Brass. (Clearance : nil.)

In order to make a detailed comparison between data from shearing and tensile tests, tensile specimens were prepared from the stocks of metals tested, and true stress/strain curves were obtained by measuring load against sectional area over the whole range to tensile fracture. These curves are shown plotted in Figs. 13–15, together with curves showing the nominal and effective shearing stresses at corresponding reductions of area in the shearing test. Here the effective stresses were obtained by dividing current shearing load by current shearing area. The points of maximum load are indicated by Δ; the curves do not extend to very large reductions, because under shear any residual load at this stage is generally associated with burnishing rather than intrinsic strength, and under tension the distribution of stress in the

small residual neck is uncertain. A comparison between the stresses at maximum load is given in Table I, both effective and nominal-stress ratios being shown.

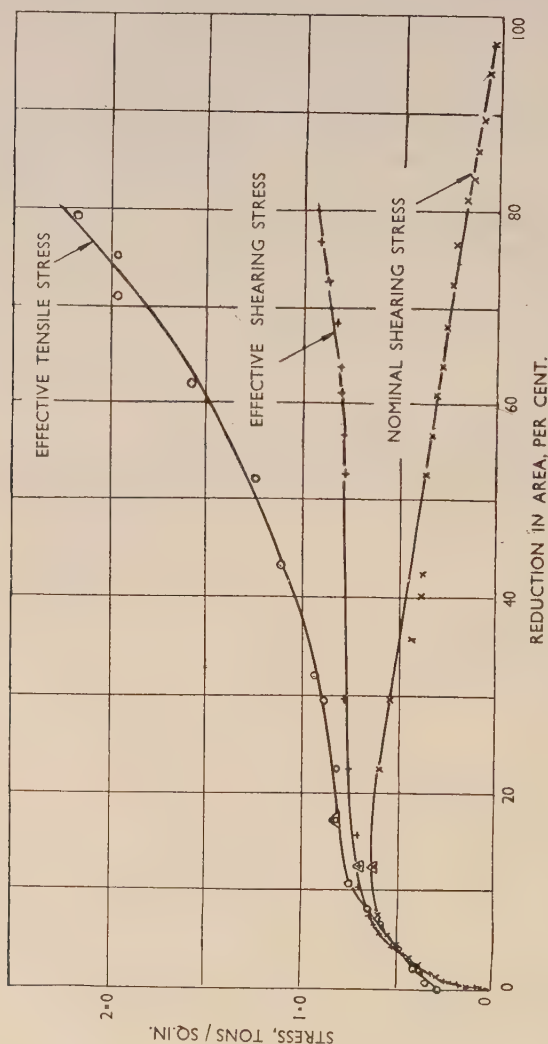


FIG. 13.—Tensile- and Shearing-Stress Curves for Lead.

Referring to the stress/strain curves it will be seen that in the case of lead (Fig. 13), the effective stress curves are very similar in shape up to about 30% reduction in area, but beyond this point the tensile-

stress curve rises steadily, while the shearing-stress curve remains practically horizontal up to about 65% reduction. Moreover, the point of maximum load occurs at about 17% reduction of area in the tensile test as against only 12.5% in shearing.

In comparing the results for copper (Fig. 14), the fact that copper (2) had been initially work-hardened is reflected in the low value of reduction at maximum load in the tensile test. But it will be noted

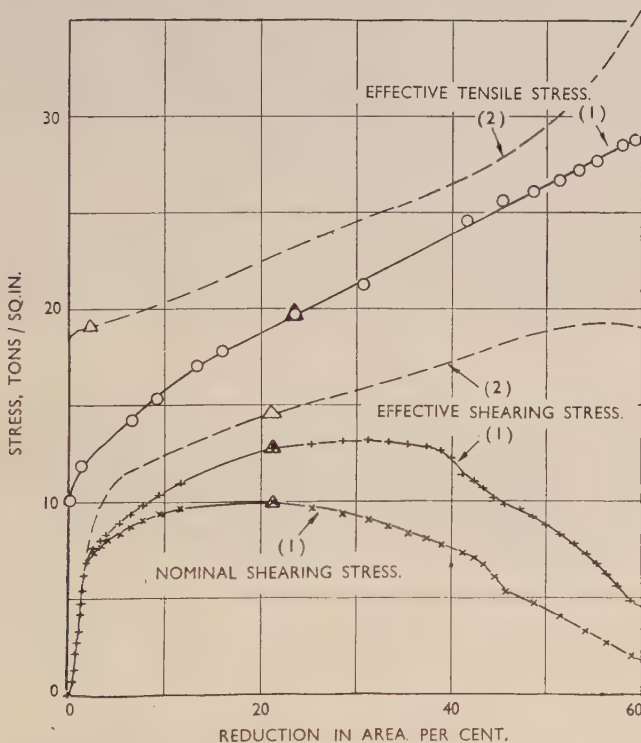


FIG. 14.—Tensile- and Shearing-Stress Curves for Copper (1) and (2).

that maximum load in the shearing operation is reached at the same "reduction" of 22% in both samples of copper, and that this reduction corresponds also to the tensile reduction of the softer copper (1). It is therefore clear that any correlation between reductions at maximum load in tension and shear must be confined to material in the annealed condition.

It will be seen from Fig. 14 that in the case of copper (1), which fails by crack propagation, the effective shear strength tends to fall away in

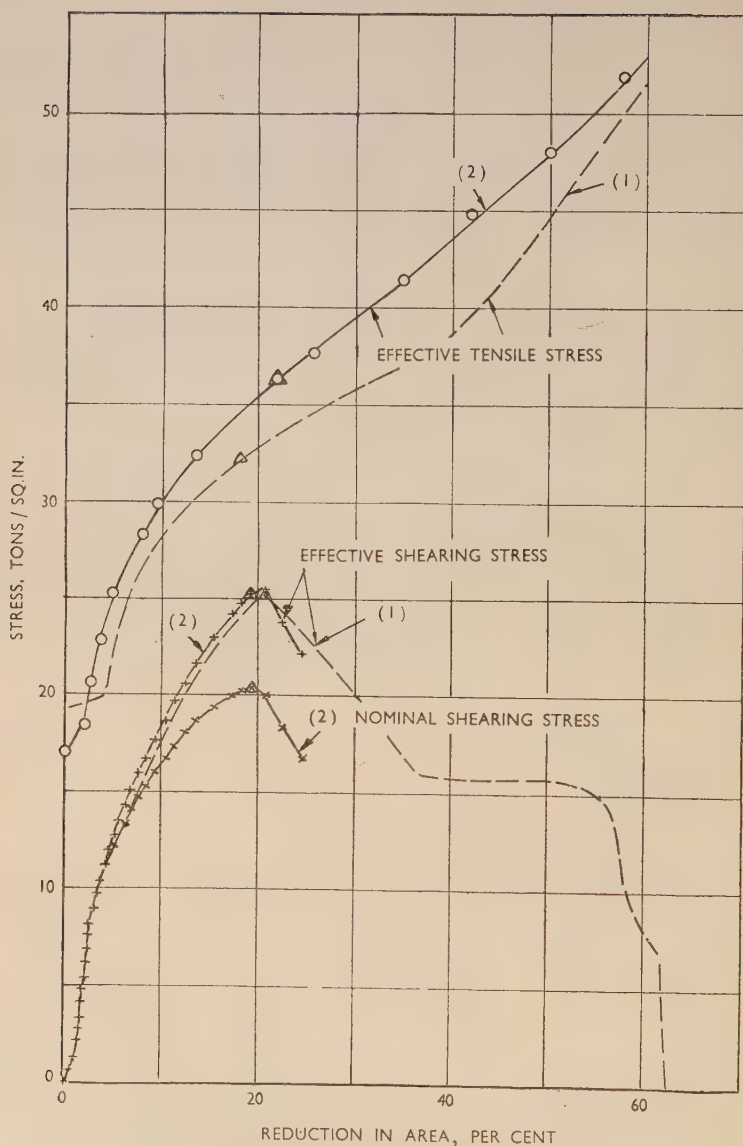


Fig. 15.—Tensile- and Shearing-Stress Curves for Mild Steel (1) and (2).

the later stages of penetration; whereas the effective strength of copper (2), which fails by true shear, continues to increase almost to the point of complete severance.

This falling away is still more marked in the case of mild steel (Fig. 15), where crack propagation is rapid when once it has begun. The tensile- and shear-stress curves follow similar trends for both stocks up to the point of maximum load, but the effective shear strength falls sharply in both cases at this point. In mild steel (1) the fall is checked by the load required to compress the tongue which forms between the cracks, while in mild steel (2) the cracks converge and final fracture rapidly supervenes.

Taking into consideration all the results obtained, there seems to be no evidence of any useful relationship between the shearing and tensile characteristics, and no possibility of predicting with confidence the magnitude or point of maximum shearing load from the results of the tensile test.

VI.—CONCLUSIONS.

From the results of the experimental work described, the following conclusions appear reasonable :

(1) There are two different modes of severance in a normal shearing operation without clearance :

(a) Ideally ductile materials suffer a bodily sliding action along the line of shear, the displaced particles maintaining their adhesion until final severance occurs at full penetration.

(b) Other materials develop cracks of tensile origin which tend to propagate at a small angle to the line of shear. If the material is sufficiently plastic these cracks propagate slowly, relieve their stress concentration by opening out, and are succeeded by others. Incipient cracks may form at free edges, which do not penetrate any depth into the material.

In less plastic materials, the cracks propagate rapidly and do not open out. Rupture will then occur either : (i) when one of the cracks has penetrated the full thickness of the metal, in which case a tongue will form between the two cracks, or (ii) when the two cracks change their course and meet each other, in which case a fairly clean rupture occurs at a relatively early stage of penetration.

(2) The provision of clearance has the effect of : (a) introducing an element of initial bending ; (b) generally increasing the volume of material involved in the process ; and (c) introducing tensile conditions in the later stages of the operation.

(3) Nevertheless, owing to the natural obliquity of incipient cracks, a clearance can be found with materials subject to crack formation,

which will cause a natural confluence of the cracks and consequently produce a clean severance with a minimum of strain work.

(4) The optimum clearances suggested for the metals tested, in the light of these considerations and the experimental results, are approximately as follows :

	Clearance, %
Lead and tin	0
Aluminium	0- 5
Copper	0-10
Brass (70 : 30	0- 5
Mild steel	5

(5) Dullness of the cutting edge has the effect of : (a) increasing the maximum shearing load, the punch penetration at maximum load, and the shearing work; and (b) increasing the size of the tongue in mild steel; aluminium is little affected in this respect.

(6) The use of negative clearance together with a die of dulled edges produces an extrusion effect, which is beneficial to the shearing of materials like aluminium in that it gives a highly polished sheared surface.

(7) Tensile overstrain raises the maximum shearing load, decreases the initial bending of the bar, and reduces the punch penetration at failure. There seems, however, little effect on the process of fracture in aluminium and brass.

(8) Attempts to correlate the stresses at maximum loads in tensile and shearing tests have produced no useful results. Whether based on true or nominal values the relationship varies from metal to metal.

ACKNOWLEDGEMENTS.

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STRESS RELIEF AND ALLIED PROBLEMS IN **1274** MAGNESIUM ALLOY CASTINGS.*

By R. J. M. PAYNE,† B.Sc., F.I.M., MEMBER.

SYNOPSIS.

A method is described by which the degree of stress relief resulting from any given annealing treatment may conveniently be assessed. The method is capable of general application to stress-relief annealing problems and has been used to establish suitable conditions of treatment for a number of magnesium- and aluminium-base casting alloys.

The problems associated with the heat-treatment of the following four Elektron casting alloys for purposes of stress removal are discussed in detail: (1) the magnesium-aluminium alloy AZ91; (2) the magnesium-aluminium alloy A8; (3) the magnesium-zinc-zirconium alloy Z5Z; (4) the magnesium-rare-earth-zirconium alloy MCZ.

It is shown that with (3) the relief of casting stresses and the precipitation-hardening of the alloy can be carried out simultaneously in a single heat-treatment. The problem of the magnesium-rare-earth-zirconium alloy is of special interest, as annealing at the temperatures customarily used for the removal of casting stresses is detrimental to the creep-resisting qualities of the alloy, which are its principal attraction.

I.—INTRODUCTION.

STRESSES may occur in castings as a result of: (1) unbalanced contraction in the mould, or (2) non-uniform cooling following heat-treatment, particularly where this involves quenching in liquids. Internal stresses arising from either of these causes may be objectionable for two reasons:

(a) When a self-stressed casting is machined, the stresses may be partially or wholly released. In extreme cases this disturbance of stress equilibrium may lead to fracture of the casting. More generally, deformation without rupture occurs and this causes considerable trouble in the machine shop; great difficulty is encountered in machining to close limits of dimensional accuracy components containing unrelieved stresses.

(b) In a casting intended to carry external loads, designed safe limits of stress may be exceeded when the normal working stresses are imposed upon static stresses already in the casting. The alternating stress which a component can safely carry is affected by the presence of static stresses, and internal stress has been recognized as a contributory factor in the premature failure of certain components subject to vibration.

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The reasons why internal stress is met with in castings and the desirability of effecting its removal are, of course, well recognized, and the interest in the subject was evident at the Institute of Metals Symposium on Internal Stresses in Metals and Alloys held in 1947.

A number of methods by which internal stress in components may be evaluated have been described in the literature; investigatory procedures of a mechanical nature were reviewed by Ford.¹ Such methods have usually been applied to wrought materials, where the investigator's interest was in the stresses induced in a part as a result of a quenching operation, or by mechanical working.

Less attention seems to have been paid to internal stress in castings, and, at the time when the present author first gave consideration to the question of stress removal (1944), no procedure for tackling such problems systematically appeared to have been worked out. A number of thermal treatments involving annealing at 250° and 300° C. were applied to production castings in magnesium alloys at the specific request of users; these treatments had the main object of avoiding distortion in machining, although the desirability of removing stresses on general grounds was also appreciated in certain quarters. Annealing conditions had been arrived at empirically, and little information was available regarding the precise effects of any given treatment. While there were no reasons for believing that magnesium alloys generally contained locked-up stresses of any great magnitude* or that the annealing treatments applied to production castings were ineffective, it was particularly important at that time to make the best possible use of the furnaces available. A principal aim of the work was, therefore, to establish a single stress-relieving heat-treatment of the shortest possible duration which could be applied effectively to all castings in the standard (magnesium-aluminium) compositions. The work carried out to rationalize procedure in respect of these alloys is described in Section III. The same method of attack was subsequently proved useful in the study of other stress-relief problems; its application to problems connected with two magnesium alloys containing zirconium is discussed in Section IV.

The work was carried out to provide information urgently needed by the production foundry, and has some shortcomings if viewed as a scientific study of stress removal. The results are, nevertheless, thought

* In support of this view it may be stated: (1) that at only slightly elevated temperatures the alloys possess a low resistance to creep, and (2) that where solution-heat-treatment processes are applied, these are normally followed by air-cooling. Even though small, such internal stresses can nevertheless produce comparatively large elastic strains on account of the low modulus of elasticity of the material (6.5×10^6 lb./in.²).

to be of interest, and the paper has been written with a two-fold objective: (1) to describe a very convenient method of establishing suitable annealing conditions for castings which is capable of general application;* and (2) to place on record the results obtained with a number of magnesium-base alloys; it may be noted here that the annealing conditions which emerged as most satisfactory for the standard magnesium-aluminium alloys have been used industrially over the past five years.

Section III, substantially as it now stands, was communicated to certain aircraft-engine builders in 1945 and to the Ministry of Supply in 1946, and reference has been made elsewhere^{3, 4} to the underlying principles on which the present work is based: no detailed test results have, however, previously been published.

II.—METHOD OF ASSESSING STRESS RELIEF.

Magnesium castings are most widely used in industry in the as-cast and in the solution-heat-treated conditions. Castings subjected to solution heat-treatment (at 415° C.) are cooled in air after removal from the furnace and are substantially free from stress. Problems of stress removal are, therefore, confined to castings which have not been solution heat-treated.

A supply of castings stressed to a uniform degree is a first requisite for a systematic study in which the efficacy of any one annealing treatment is to be compared with that of any other. A direct method of attack would be to produce test castings so shaped as to develop internal stress on cooling in the mould. It was, however, thought very unlikely that any such method would yield consistent results, as the initial values of stress (which would be affected by variations in mould and casting conditions) would not be sufficiently under control and not be ascertainable in the castings actually used for stress-relief tests. It was considered preferable to take initially stress-free sand castings and to impose the required stresses upon them by straining to a controlled degree. The extent to which the known strain was subsequently relieved by annealing would be taken as a measure of the suitability of the heat-treatment conditions for the intended purpose. It was assumed that any observations and conclusions based upon test specimens artificially stressed in this way would hold equally well for castings in which the stresses had been developed by unbalanced contraction in the mould.

The form of test casting adopted is shown in Fig. 1. In carrying

* The same principle has recently been used by Hallett and Wing² for studying stress-relief problems in cast iron.

out tests a stock of ring castings was first prepared, the metal being cast in green-sand moulds under careful control. Fig. 2 (Plate XXIX) shows a spray of such castings. After the removal of runners and risers the test rings were cut with a circular saw (see Fig. 1), particular care being taken to avoid distortion in clamping the castings to the table of the milling machine. Castings made in this way are substantially stress-free or, at least, in stress equilibrium, as is proved by the fact that no appreciable movement occurs on sawing through the ring.

Gauge marks were scribed upon the two sides of the casting at the points shown. The pieces were then stressed by the forcible insertion into the gap of a "wedge" (actually a piece of steel $\frac{3}{16} \pm 0.0005$ in. thick, tapered at one end). The magnitude of the stresses developed

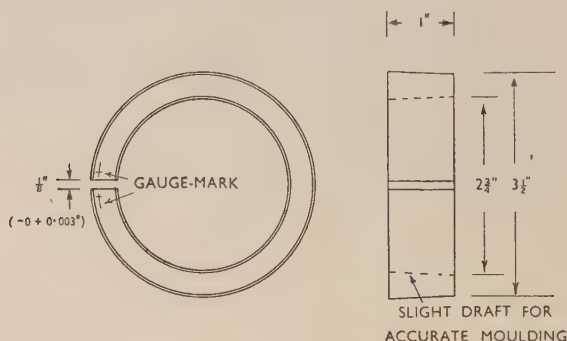


FIG. 1.—Ring Test Casting.

in this way is not accurately known,* but this was not a cause for any deep concern, as subsequent tests (described in Section III. 2) showed that residual stresses were largely independent of initial stresses. It was, however, observed that the insertion of the $\frac{3}{16}$ -in. wedge caused a very small permanent set, and from this it was deduced that the skin stress at the point of maximum bending moment must have been greater than that corresponding to the limit of proportionality of the material (approximately 1.6 tons/in.² for the standard casting alloys).

Sets of rings were annealed in a tubular electric furnace at the required temperatures with the steel "wedges" in place, then carefully removed and allowed to cool in still air with the wedges in position. When

* At a later date the skin stresses developed in a ring casting by the insertion of a $\frac{3}{16}$ -in. wedge were evaluated, using an electric-resistance strain-gauge. A strain of 0.093%, corresponding in the AS alloy to an applied stress of 2.3 tons/in.², was deduced from these measurements.



FIG. 2.—Spray of Ring Test Castings.

[To face p. 150.]

cold, the distance between the gauge marks was measured using a Cambridge travelling microscope. The wedges were then removed and a further measurement made. The "spring-back" was taken as a measure of the remanent stress in the ring, and it is with this remanent

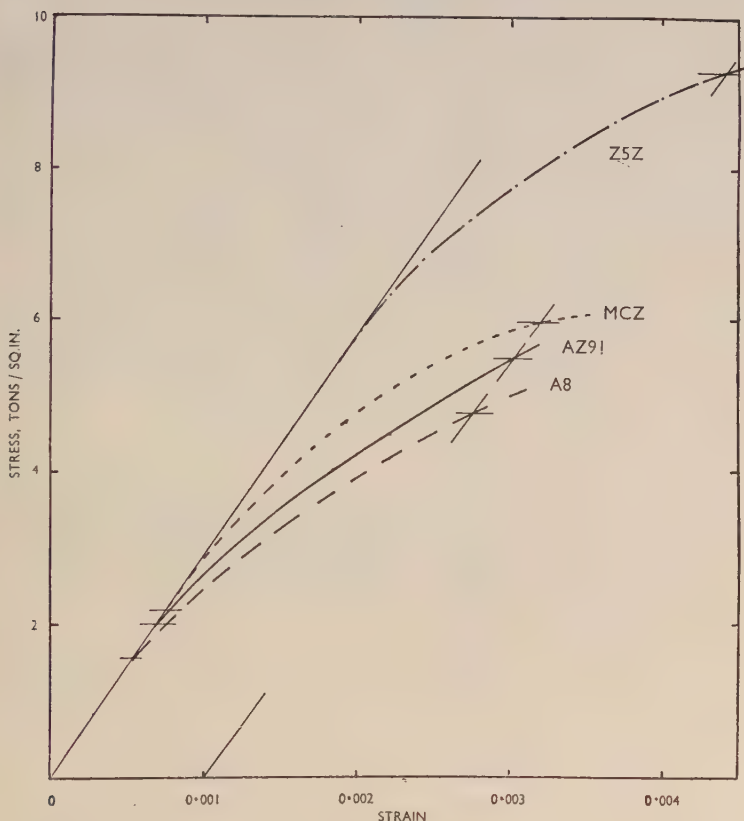


FIG. 3.—Stress/Strain Characteristics of A8, AZ91, MCZ, and Z5Z Alloys.

Modulus of elasticity = 6.5×10^4 lb./in.²

stress (a point of principal interest to the user of castings) that the author was mainly concerned. In some circumstances it was, however, of interest to express the degree to which stress was relieved by a given annealing treatment, and a value for percentage stress removal was deduced from the initial and final strains, an allowance being made for

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TABLE I.—*Stress Relief in AZ91 Ring Castings Resulting from Various Annealing Treatments.*

Analysis : Aluminium 9·78, zinc 0·51, manganese 0·22, copper 0·01, silicon 0·05, iron 0·03%, magnesium remainder.

Initial strain at gap = 1·588 mm. (wedge $\frac{3}{16}$ in. thick in $\frac{1}{8}$ in. gap).

Temperature, ° C.	Annealing Time, hr.	Distance between Gauge Marks after Annealing, mm.		Spring-Back, mm.*	Mean Spring- Back, mm.
		Wedge in *	Wedge removed*		
250	$\frac{1}{2}$	9·250 9·268	8·801 8·826	0·449 0·442	0·446
	1	9·262 9·266	8·936 8·939	0·326 0·327	0·327
	2	9·273 9·249	9·005 8·979	0·268 0·270	0·269
	4	9·738 9·603	9·535 9·397	0·203 0·206	0·205
	8	9·314 9·295	9·174 9·157	0·140 0·138	0·139
	24	9·357 9·276	9·253 9·168	0·104 0·108	0·106
	72	9·330 9·309	9·273 9·248	0·057 0·061	0·059
	144	9·296 9·287	9·241 9·224	0·055 0·063	0·059
300	$\frac{1}{2}$	9·259 9·234	9·071 9·045	0·188 0·189	0·189
	1	9·271 9·262	9·118 9·104	0·153 0·158	0·156
	2	9·234 9·246	9·126 9·122	0·108 0·124	0·116
	4	11·811 9·233	11·725 9·148	0·086 0·085	0·086
	8	9·265 9·236	9·197 9·163	0·068 0·073	0·071
	24	9·249 9·260	9·203 9·211	0·046 0·049	0·048
	72	9·272 9·313	9·231 9·275	0·041 0·038	0·040
	144	11·506 9·245	11·480 9·215	0·026 0·030	0·028

TABLE I.—Continued.

Temperature, °C.	Annealing Time, hr.	Distance between Gauge Marks after Annealing, mm.		Spring-Back, mm.*	Mean Spring- Back, mm.
		Wedge in *	Wedge removed*		
330	$\frac{1}{2}$	9.251 9.223	9.112 9.093	0.139 0.130	0.135
	1	9.121 9.241	9.022 9.148	0.099 0.093	0.096
	2	9.268 9.307	9.196 9.231	0.072 0.076	0.074
	4	9.208 9.273	9.159 9.231	0.049 0.042	0.046
	8	9.634 9.658	9.593 9.616	0.041 0.042	0.042
	24	9.655 9.243	9.621 9.208	0.034 0.035	0.035
	72	9.252 9.307	9.213 9.265	0.039 0.042	0.041
	144	9.315 9.311	9.291 9.282	0.024 0.029	0.027

* The two values given in these columns for each annealing time represent measurements made on the two sides of one and the same casting.

the small permanent set which occurred through stressing the material beyond the elastic limit.

It may be of interest in reading the paper to refer to stress/strain curves of the materials under consideration which are given in Fig. 3.

III.—STANDARD CASTING ALLOYS AZ91 AND A8.

1. Stress Relief at 250°, 300°, and 350° C. with Uniform Initial Applied Stress.

At the time when the investigatory work was undertaken, annealing treatments were called for by two users of magnesium castings. User "A" required castings to be annealed for 4 hr. at 250° C.; user "B" specified 4 hr. at 300° C. Tests were therefore carried out on specimens annealed for various periods at 250° and 300° C., and these indicated that the better results were obtained using the higher temperature; further tests were therefore made at 330° C.—the highest treatment temperature possible if solution of Mg_4Al_3 is to be avoided. The com-

TABLE II.—*Stress Relief in A8 Ring Castings Resulting from Various Annealing Treatments.*

Analysis : Aluminium 8.29, zinc 0.66, manganese 0.22, copper 0.05, silicon 0.02, iron 0.06%, magnesium remainder.

Initial strain at gap = 1.588 mm. (wedge $\frac{3}{16}$ in. thick in $\frac{1}{8}$ in. gap).

Temperature, ° C.	Annealing Time, hr.	Distance between Gauge Marks after Annealing, mm.		Mean Spring- Back, mm.
		Wedge in *	Wedge removed*	
250	1	10.075 10.115	9.745 9.78	0.3325
	2	10.12 10.11	9.815 9.80	0.3075
	4	10.085 10.125	9.87 9.91	0.215
	16	10.025 10.085	9.86 9.91	0.170
	64	10.05 10.01	9.975 9.94	0.0725
300	$\frac{1}{2}$	10.00 9.95	9.785 9.735	0.215
	1	9.99 9.96	9.82 9.795	0.1675
	2	9.98 9.975	9.83 9.825	0.15
	4	10.00 10.00	9.90 9.90	0.10
	8	9.96 9.965	9.885 9.89	0.075
	16	9.92 10.025	9.855 9.955	0.0675
330	$\frac{1}{2}$	9.97 9.91	9.84 9.77	0.135
	1	9.99 10.03	9.89 9.93	0.10
	2	9.96 9.99	9.87 9.90	0.09
	4	9.98 10.02	9.92 9.96	0.06
	8	9.95 9.91	9.91 9.86	0.045

TABLE II.—*Continued.*

Temperature, ° C.	Annealing Time, hr.	Distance between Gauge Marks after Annealing, mm.		Mean Spring- Back, mm.
		Wedge in *	Wedge removed*	
330	16	10.015	9.975	0.045
		10.005	9.995	
	32	9.813	9.776	0.039
		9.796	9.755	
	72	9.699	9.673	0.030
		9.803	9.769	
	144	9.584	9.58	0.006
		9.60	9.592	

* The two values given in these columns for each annealing time represent measurements made on the two sides of one and same casting.

position of the materials used is given at the head of Tables I and II. The results of the three stress-relief tests—all made using a $\frac{3}{16}$ -in. wedge—are given in Table I and Fig. 4 for AZ91 (to D.T.D. specification No. 136B), and in Table II and Fig. 5 for A8 (to D.T.D. specification No. 59B).

It will be observed that the removal of stress proceeds rapidly in the early stages of annealing and at a diminishing rate thereafter. The three curves tend to become parallel to the time axis at three different levels, indicating that relaxation proceeds until stress is reduced to a limiting value which depends on the temperature of test. The annealing temperature is the most important factor in the process, and it is more advantageous to increase the temperature than to prolong the time of annealing.

Two points of practical importance emerged from this work: (1) The 4-hr. treatment at 250° C. (*A*) was less effective than that at 300° C. (*B*) and removed only about 87% of the stress initially present; the same result could have been achieved in about $\frac{1}{2}$ -hr. at 300° C., or in even less time at 330° C.

(2) The same degree of stress removal as was secured by treatment *B* could be obtained in 2 hr. by raising the temperature 30° C., such treatment removing about 95% of the initial stress.

2. Stress Removal with Stresses of Different Magnitude.

The tests described above indicated the advantages of carrying out the annealing treatment at higher temperatures than had hitherto been

employed for production castings and showed a temperature of 330° C. to be favourable for achieving the desired result. It was decided next to investigate by tests carried out at this temperature whether the actual magnitude of the imposed stresses had any bearing upon the magnitude of the residual stresses after a particular annealing treatment.

Stresses both greater and smaller than those produced by means of the $\frac{3}{16}$ -in. wedge were applied. The material employed was A8 and the same form of test casting was used. A number of rings were prepared and strained to different degrees by the insertion of wedges

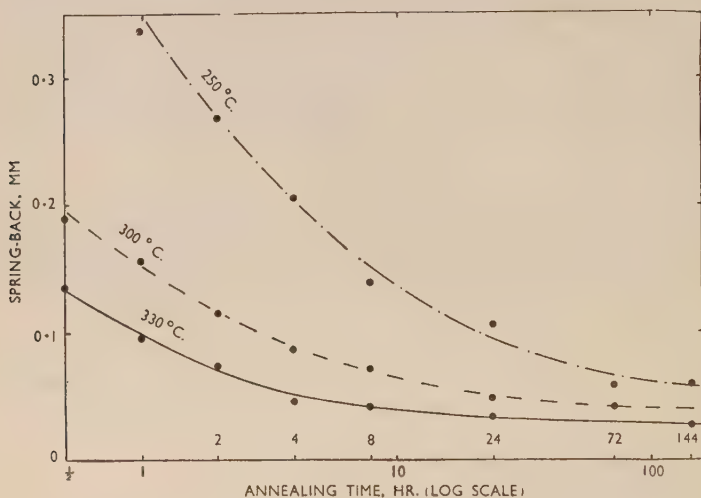


FIG. 4.—Stress-Removal Test Results on AZ91. Initial strain at gap 1.588 mm. (wedge $\frac{3}{16}$ in. thick in $\frac{1}{8}$ in. gap).

$\frac{5}{32}$, $\frac{1}{4}$, $\frac{3}{8}$, and $\frac{1}{2}$ in. thick. Annealing was carried out at 330° C. for periods of 2 and 8 hr. As before, measurements of the extent of the spring-back upon removal of the wedge was taken as an indication of the magnitude of the remanent stress. The results are given in Table III.

It will be seen that after 2 hours' treatment at 330° C. the spring-back is of the same order (0.06–0.11 mm.) with specimens strained by the insertion of wedges ranging from $\frac{5}{32}$ to $\frac{1}{2}$ in. in thickness; variations from specimen to specimen appear to be of no particular significance and the elastic movement with all test-pieces is small. Remanent stresses after 8-hr. treatments are again independent of the thickness

of the wedge, and of a lower order than with 2-hr. treatments. The spring-back observed with all specimens is small, and it appears clear that any annealing treatment capable of removing small stresses (of the order of the stress corresponding to the limit of proportionality of the material *) would suffice to remove any greater stresses which might be present.

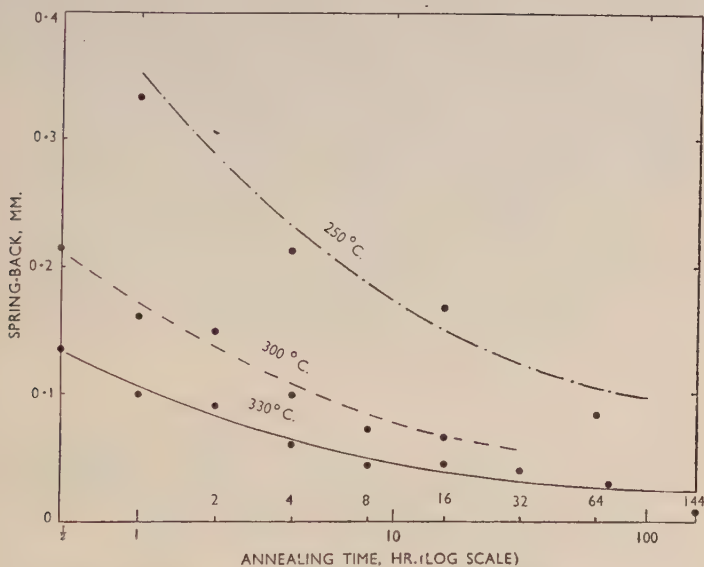


FIG. 5.—Stress-Removal Test Results* on A8. Initial strain at gap 1.588 mm. (wedge $\frac{3}{16}$ in. thick in $\frac{1}{8}$ in. gap).

3. Effect of Annealing Treatments on Mechanical Properties.

The influence of annealing treatments at 250°, 300°, and 330° C. upon the mechanical properties of sand-cast D.T.D. test-bars of AZ91 and A8 is shown in Tables IV and V, respectively. The mechanical characteristics of bars from the same melt, but in the as-cast condition, are given for purposes of comparison.

It will be seen that for all three temperatures and for both alloys the annealing treatments are without very marked effect upon mechanical properties. The ultimate tensile strength is in some cases increased by about 1 ton/in.² as a result of heat-treatment. Precipita-

* As in the specimen stressed with the $\frac{5}{32}$ -in. wedge.

tion-hardening causes an increase in the 0.1% proof stress and some loss of ductility, these effects being most pronounced in the material annealed at 250° C. and least marked in that treated at 330° C.

TABLE III.—*Effects of Variation of Imposed Stresses on Residual Stresses in A8 Ring Castings Annealed at 330° C.*

Annealing Time, hr.	Thickness of Wedge, in.	Distance between Gauge Marks before Annealing, mm.			Permanent Set before Annealing, mm.	Distance between Gauge Marks after Annealing, mm.		Mean "Spring-back", mm.
		No wedge *	Wedge in *	Wedge removed *		Wedge in *	Wedge removed *	
2	$\frac{5}{32}$	8.141 8.156	8.940 8.977	8.161 8.181	0.019	8.944 8.972	8.874 8.903	0.070
	$\frac{3}{16}$	0.090†
	$\frac{1}{4}$	8.149 8.160	11.523 11.620	8.635 8.645	0.473	11.514 11.587	11.451 11.531	0.060
	$\frac{3}{8}$	8.112 8.123	15.006 15.13	9.50 9.52	1.388	15.03 15.10	14.92 14.99	0.11
	$\frac{1}{2}$	8.056 8.145	18.17 18.42	...	2.585	18.15 18.36	18.06 18.27	0.09
8	$\frac{5}{32}$	8.118 8.158	8.812 8.993	8.132 8.175	0.019	8.804 9.004	8.869 8.966	0.037
	$\frac{3}{16}$	0.045†
	$\frac{1}{4}$	8.149 8.151	11.685 11.635	8.613 8.607	0.473	11.720 11.635	11.662 11.588	0.053
	$\frac{3}{8}$	8.012 7.963	14.87 14.77	9.40 9.24	1.388	14.872 14.750	14.818 14.702	0.051
	$\frac{1}{2}$	8.095 8.145	18.30 18.51	10.67 10.74	2.585	18.21 18.475	18.17 18.42	0.048

* The two values given in these columns for each annealing time represent measurements made on the two sides of one and the same casting.

† Values for $\frac{3}{16}$ -in. wedge taken from Table II.

4. Conclusions.

The measurements of stress in ring test castings of A8 and AZ91 have indicated the general relationship between initial stress, annealing time and temperature, and remanent stress. The degree of stress relaxation that will occur when a self-stressed casting is annealed will be determined by the creep behaviour of the material. For any annealing

temperature chosen the material will possess a limiting value for creep stress and, however long the annealing may be continued, the remanent stress can never fall below this value. Since for the materials in question the creep strength falls off sharply as the temperature rises above 250° C., there is every reason for using these higher temperatures.

TABLE IV.—*Effects of Various Annealing Treatments on Mechanical Properties of AZ91 Sand-Cast D.T.D. Test-Bars.*

Analysis : Aluminium 9.24, zinc 0.48, manganese 0.21, copper 0.03, silicon 0.07, iron 0.03%, magnesium remainder.

Temperature, ° C.	Annealing Time, hr.	0.1% Proof Stress,* tons/in. ²	Ultimate Tensile Stress,* tons/in. ²	Elongation,* %
250	As cast	6.8	10.2	1.6
	2	7.6	10.7	1.0
	4	7.5	10.9	1.0
	8	7.5	10.9	0.8
	16	7.4	11.2	1.1
300	1	7.2	10.7	1.0
	2	7.3	11.0	1.0
	4	7.5	11.1	1.25
	8	7.4	10.5	0.92
	16	7.2	10.3	1.08
330	1	7.2	10.6	1.25
	2	7.2	10.7	1.08
	4	7.0	10.1	0.92
	8	6.7	10.4	1.42

* The figures represent the mean values of tests on three or more test-bars.

A 2-hr. annealing treatment at 330° C. was shown by the work described to give a large measure (approximately 95%) of stress relief without detriment to the mechanical properties of the material, with an appreciable saving in time by comparison with the treatments then in use.* Such a treatment has therefore been regularly applied to production castings for purposes of stress relief since 1944.

* Provided that a furnace capable of raising the casting quickly to the annealing temperature is available. Gas-heated furnaces of the type in which the combustion gases circulate over the furnace charge fulfil this requirement.

As a matter of interest, an attempt was made to evaluate the stresses left in a ring casting after such an annealing treatment. By attaching an E.R. strain-gauge to a ring casting at a point diametrically opposite to the gap, the surface strains occurring when the gap was forced open by known amounts were determined experimentally. From these observations and a knowledge of stress/strain characteristics of the

TABLE V.—*Effects of Various Annealing Treatments on Mechanical Properties of A8 Sand-Cast D.T.D. Test-Bars.*

Temperature, ° C.	Annealing Time, hr.	0.1% Proof Stress,* tons/in. ²	Ultimate Tensile Stress,* tons/in. ²	Elongation,* %
250	As cast	6.0	10.5	2.8
	2	7.2	10.8	1.75
	4	7.05	10.95	2.0
	8	6.9	10.75	1.5
	16	7.3	10.95	2.0
300	2	6.4	10.8	2.25
	4	6.37	10.9	2.37
	8	6.5	10.6	2.5
330	1	6.85	10.85	2.0
	2	6.8	10.8	2.5
	4	6.5	10.95	2.75
	8	6.55	11.1	3.0

* The figures represent the mean values of tests on two or more test-bars.

material it was concluded that the value for spring-back obtained after annealing A8 and AZ91 for 2 hr. at 330° C. (roughly 0.08 mm.) corresponded to skin stresses of about 0.13 tons/in.²; this value therefore represents the maximum stress likely to be found in an annealed casting.

IV.—MAGNESIUM ALLOYS CONTAINING ZIRCONIUM.

1. *Magnesium-Zinc-Zirconium Alloy (Elektron Z5Z).*

The development of the casting alloy Elektron Z5Z, containing 4.5% zinc and 0.7% zirconium has been described elsewhere.⁵ This

alloy is generally used in the heat-treated condition, as this yields the high value for proof stress which makes the material attractive to designers; sand-cast D.T.D. test-bars thus treated show the following values in a tensile test:

0.1% Proof stress	.	.	.	✂	8.5 tons/in. ²
Ultimate stress	.	.	.	✂	15 "
Elongation	.	.	.	✂	5%

This alloy was first made available in production quantities in 1946, a heat-treatment of 24 hours' duration at 180° C. being recommended for the development of the full properties.

Creep tests made earlier,⁶ had shown that the behaviour of a magnesium-zinc-zirconium alloy containing 3% zinc at 200° C. was comparable with that of the standard magnesium-aluminium alloy A8, and there were no reasons for expecting that Z5Z, with its higher zinc content, would behave very differently. The tests described in Section III had proved that 250° C. was too low a temperature for effective stress removal with A8, and it could not, therefore, be expected that heat-treatment of Z5Z at 180° C. (as recommended for the development of the optimum mechanical properties), would do much to relieve stresses present in castings as a result of unbalanced contraction. It was apparent, therefore, that if components were to be supplied in a stress-free condition, other conditions of heat-treatment had to be found. A further incentive arose from the need of the production foundry for a method of "setting" castings by heating.*

It was known that the heat-treatment of magnesium-zinc-zirconium alloy at temperatures of the order of 415° C. (as ordinarily used for setting castings) was prejudicial to the development of the highest proof stress, and some lower temperature had to be sought. The possibility of carrying out the operation in the furnace used for the stress-relief annealing of castings in the standard magnesium-aluminium alloys was attractive, and the effect of annealing Z5Z at 330° C. was accordingly investigated. The mechanical properties of sand-cast test-bars, heat-treated for 1-6 hr. at that temperature are given in Table VI. It will be seen that the full proof stress of the material is developed in a

* With certain classes of work of medium or large size but of thin wall-section, e.g. aircraft window and door frames, close limits of dimensional accuracy are difficult to attain in castings as taken from the mould. In such cases it may be expedient to heat-treat the part on an accurately shaped jig, at a temperature such as will cause the casting to yield plastically under applied weights; in this way the part may be made to assume the shape of the jig and troublesome warpage corrected. With the ordinary alloys this "setting" of castings is usually carried out in a solution-heat-treatment operation at 415° C., as the type of work to which it is applied is generally called for in the homogenized condition.

heat-treatment of 2 hr., i.e. the same duration as for the stress-relief annealing of the standard alloys. Practical tests with shaped castings showed that components could be "set" using a 2-hr. treatment at 330° C., and stress-relief tests with ring specimens confirmed that the

TABLE VI.—*Mechanical Properties of Z5Z Sand-Cast D.T.D. Test-Bars Heat-Treated at 330° C.*

Time of Treatment, hr.	0.1% Proof Stress,* tons/in. ²	Ultimate Tensile Stress,* tons/in. ²	Elongation,* %
1	9.1	17.6	10
1½	9.1	17.9	11
2	9.6	17.7	9.5
4	8.7	17.5	10
6	8.8	17.5	11

* The figures represent the mean value for two or more test-bars.

same process was effective for stress-removal purposes, some 97.5% of the initial strain being removed. The 2-hr. treatment at 330° C. was therefore adopted for use in the foundry on production castings.*

2. *Magnesium-Rare-Earth-Zirconium Alloy (Elektron MCZ.)*

Magnesium-rare-earth-zirconium alloys, with or without additions of other metals such as zinc, are important by reason of their good resistance to creep at temperatures of the order of 200° C.⁶ MCZ (nominal composition 3% Mischmetall, 0.6% zirconium, remainder magnesium) shows the following mechanical properties in the standard D.T.D. pattern sand-cast test-bar :

0.1% Proof stress	.	.	.	5.5-6.5 tons/in. ²
Ultimate stress	.	.	.	9.5-10.5 "
Elongation	.	.	.	4-6%

It became necessary to investigate problems relating to the release of internal stress in connection with large compressor castings in this alloy supplied for use with gas turbines.

* At a later date Magnesium Elektron, Ltd., pointed out some advantages in a two-stage heat-treatment. By heating the castings to 180° C. for 24 hr. after annealing at 330° C., slightly better mechanical properties can be secured than are obtainable by any single treatment. The low-temperature treatment does not re-introduce stresses, and castings dealt with in this way are therefore substantially stress-free. The two-stage heat-treatment is now standard practice.

It was appreciated that, in this instance, and in contrast with A8, AZ91, and Z5Z, a material was concerned whose particular virtue—its resistance to creep—would tend to render less effective any annealing treatment applied for purposes of stress-relief. Creep tests made earlier at 250° C. had, however, indicated that creep-resistance diminished rather sharply when temperatures of 200° C. were exceeded, and it appeared reasonable to expect that an annealing treatment at the standardized temperature (330° C.) would again prove effective in removing stress. Before studying stress-removal effects, however, the influence of the 2 hr. treatment at 330° C. upon the creep properties of

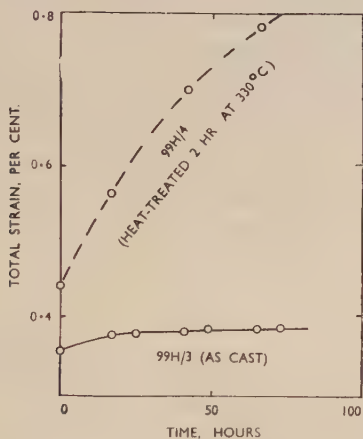


FIG. 6.—Creep Test Results at 200° C. on MCZ, showing detrimental effects of annealing at 330° C. Load 4 tons/in.²

MCZ was investigated, as it was suspected from other work that the ability of the material to withstand sustained stress might be adversely affected by high-temperature annealing.

The composition as determined by analysis, and the mechanical properties at ordinary temperatures of the MCZ alloy used for the creep and stress-relief tests referred to in this Section are given in Table VII.

The results of a tensile creep test at 4 tons/in.² upon the alloy (a) in the as-cast condition (as normally used) and (b) after stress-relief treatment, are given in Fig. 6, and it will be seen that the creep-resistance of the material has been seriously impaired by annealing. This creep test and others subsequently referred to were all carried out at 200° C., and the values for strain plotted in curves represent the sum of the elastic and plastic components, neither of which was determined

separately; specimens were held at temperature for 20 hr. before the load was applied.

The adverse effects of annealing at 330° C. are no less marked in comparative creep tests with as-cast and annealed material, carried out at a reduced stress of 3 tons/in.², and are still evident in the results of the test at only 2 tons/in.² (Fig. 7). As stresses of the order of 2–3 tons/in.² might well be applied to a casting in service, it was clear that stress-relief treatment at 330° C. was unsuitable for parts for which a good resistance to creep was important; it may be noted in passing that treatment at 330° C. was without appreciable influence upon the mechanical properties of the material at ordinary temperatures or apparently upon its microstructure.

Tests were now undertaken to determine whether any useful degree of stress relief could be obtained at temperatures lower than 330° C., and curves obtained by annealing ring castings at 300°, 250°, and 200° C. are given in Fig. 8. It will be seen that annealing at 300° C.

TABLE VII.—*Composition and Mechanical Properties at Ordinary Temperatures of MCZ Alloy.*

Melt No.	Rare Earth Content (by analysis), %	Alloy used for :	Mechanical Properties (D.T.D. sand-cast test-bar)		
			0.1% Proof Stress, tons/in. ²	Ultimate Stress, tons/in. ²	Elongation, % on 2 in.
99H	2.93	Creep test (Fig. 6)	6.6	10.4	6
56L	2.34	Creep test (Fig. 7)	6.2	10.4	7.5
95L	2.91	Creep test (Fig. 7)	6.2	10.4	7
50M	3.59	Stress-relief test (Fig. 8)	6.5	11.0	8.5
P68C	3.4	Creep test (Fig. 9)	6.6	10.7	6
P51	3.44	Creep test (Fig. 10)	6.3	10.6	7.5

for about 10 hr. has an appreciable effect on internal stress, although stresses are not reduced to the same low level with MCZ as with the standard alloys (cf. Fig. 8 with Figs. 4 and 5). Annealing at 250° C. is much less effective than annealing at 300° C., and treatment at 200° C. produces no worth-while result.

Tests on MCZ annealed for 10 hr. at 300° C. showed that treatment at this temperature had the same harmful effect on creep-resistance as annealing at 330° C., and was therefore inadmissible for parts required to

withstand steady stress. Specimens annealed for 10 hr. at 250° C. showed creep-resisting properties comparable with the as-cast alloy when tested at 3 tons/in.² (Fig. 9). Annealing at 250° C. could therefore be accepted as a means of reducing stresses in castings without interfering with creep properties; the degree of stress relief achieved by such a treatment is, however, small. From Fig. 8 it will be seen that a spring-back of 0.79 mm. was observed with a ring specimen annealed for 10 hr. at 250° C., and E.R. strain-gauge experiments showed that a strain of this magnitude corresponded with a surface stress of 1.2 tons/in.² at a point opposite the gap. It would seem therefore that

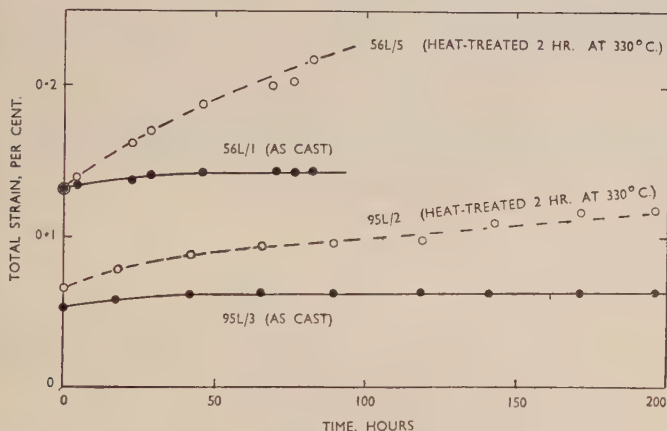


FIG. 7.—Creep Test Results at 200° C. on MCZ. Two upper curves: load 3 tons/in.²; lower curves: load 2 tons/in.²

remanent stresses as high as 1.2 tons/in.² may be encountered in MCZ castings heat-treated under these conditions.

In recently published work Mellor and Ridley⁷ reported that solution-heat-treated wrought magnesium-rare-earth alloys showed a good resistance to creep, and were much superior in this respect to alloys in the as-wrought or wrought-and-annealed conditions. In other words, they demonstrated that the good resistance to creep of rare-earth-bearing alloys is attributable to the rare earths held in solid solution in the magnesium or existing as a fine precipitate. The results of a test made with the magnesium-rare-earth-zirconium alloy MCZ (a) as cast, (b) as solution heat-treated (24 hr. at 570° C.), and (c) as solution-treated and aged 24 hr. at 200° C. are given in Fig. 10. It will be seen that both the solution-treated and the solution and precipitation heat-treated

specimens show creep rates of a low order, comparable with those of the cast material. In making comparisons between the creep curves given in Fig. 10 it should be borne in mind that although specimens were nominally in the as-cast, solution heat-treated, and solution and precipitation heat-treated conditions, the method of testing (by which all specimens were maintained at temperature for 20 hr. before application of load) provided opportunities in all cases for precipitation-hardening to occur; in point of fact, therefore, all specimens were tested in the aged condition.

A test on a MCZ ring casting annealed at 570° C. and air-cooled showed this to be free from stress.

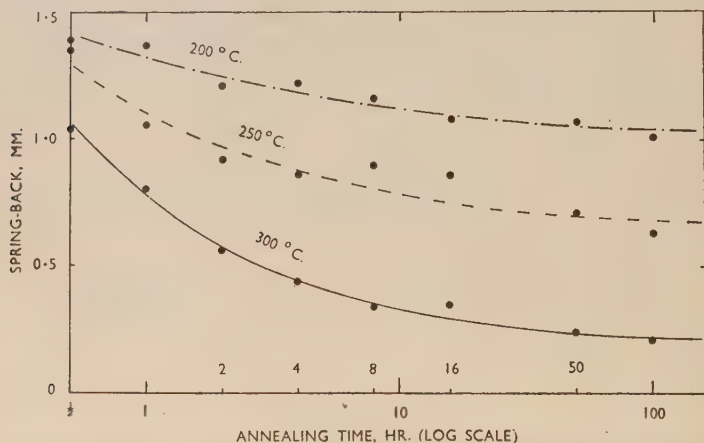


FIG. 8.—Stress-Removal Test Results on MCZ (Melt No. 50M). Initial strain at gap 1.588 mm. (wedge $\frac{3}{16}$ in. thick in $\frac{1}{8}$ in. gap).

The conclusions drawn from the work on the MCZ alloy may be summarized as follows :

(1) Where the shape of the castings is such that they would not be expected to contain large locked-up stresses, and for those applications where small dimensional changes resulting from the release of internal stress could be tolerated, the alloy is best left in the as-cast condition.

(2) A small measure of stress relief can be secured by annealing castings for about 10 hr. at 250° C., and such treatment will have no detrimental effect on creep behaviour at 200° C. Stresses will not be reduced to a particularly low value by annealing at 250° C., and the treatment may not prevent some distortion occurring on machining the component. The finished casting will, nevertheless, have been stabilized, and no further changes of dimensions should occur in service

at 200° C. Annealing at temperatures higher than 250° C. seriously affects creep strength at 200° C., and temperatures lower than 250° C. are ineffective in removing internal stress.

(3) Where it is imperative that castings should be free from locked-

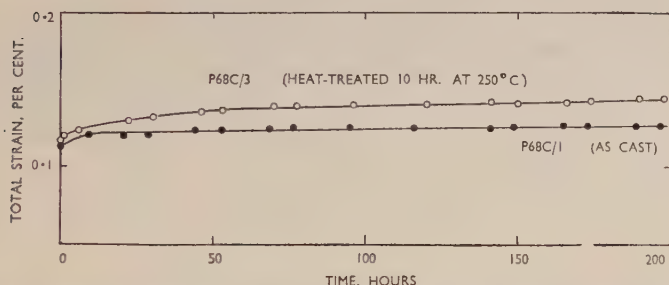


FIG. 9.—Creep Test Results at 200° C. on MCZ, showing that annealing at 250° C. has no serious adverse effects upon its behaviour. Load 3 tons/in.²

Creep rate at 120 hr.: as-cast = 0.25×10^{-6} strain/hr.
 heat-treated = 0.5×10^{-6} „

upstresses, a high-temperature solution-treatment (at 570° C.) is possible; the castings would be cooled in air at the conclusion of the solution-treatment to avoid the re-introduction of stress (through unbalanced cooling) which would occur in a quenching operation. From the

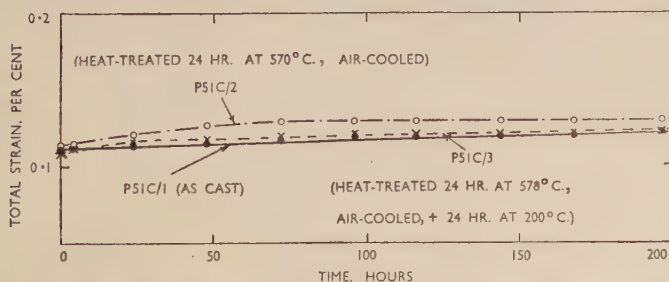


FIG. 10.—Creep Test Results at 200° C. on MCZ, showing effects of solution and solution + precipitation heat-treatments. Load 3 tons/in.²

present tests there would appear to be some but not much advantage in heat-treating castings at 200° C. following the solution-treatment, but further experience is required to show whether either the solution-treatment or the double-stage heat-treatment, with the additional trouble, expense, and risk of distortion involved, could justifiably be

applied to castings for stress-removal purposes. It may be added that earlier work ⁶ has shown that the mechanical properties of MCZ are not appreciably changed by heat-treatment.

ACKNOWLEDGEMENTS.

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THE EFFECT OF SMALL QUANTITIES OF Cd, 1275 In, Sn, Sb, Tl, Pb, OR Bi ON THE AGEING CHARACTERISTICS OF CAST AND HEAT- TREATED ALUMINIUM-4% COPPER-0.15% TITANIUM ALLOY.*

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SYNOPSIS.

It has recently been shown that tin is slightly soluble in aluminium and that tin additions have a pronounced influence on precipitation effects in commercial-purity aluminium-4½% copper alloys (Sully, Hardy, and Heal, *J. Inst. Metals*, 1949-50, 76, 269). This work has now been extended to the aluminium-4% copper-0.15% titanium alloy of very high purity containing elements adjacent to tin in the Periodic Table.

Evidence for the solubility of these elements in aluminium has been obtained from the age-hardening behaviour of the binary alloys following solution heat-treatment. The solid solubilities at 530° C. of cadmium, indium, and tin in aluminium are judged to be of the order of 0.05-0.1 wt.-%, whilst the solubilities of antimony, thallium, lead, and bismuth are taken to be negligibly small at this temperature.

Small quantities of the order of 0.05 wt.-% (0.012 at.-%), of cadmium, indium, or tin have a definite influence on the course of precipitation of copper in aluminium. The natural ageing is depressed, but the rate of artificial ageing is accelerated by a factor between three and eight. Both the response to artificial ageing and the absolute strength are increased.

The insoluble elements, antimony, thallium, lead, and bismuth, have no influence on the ageing of the aluminium-copper alloy, although the bismuth particles mechanically reduce the strength properties.

Very small additions of magnesium, of the order of 0.06%, greatly diminish the influence of indium or tin, but do not affect the alloys containing cadmium. The quantity of magnesium required to neutralize the influence of indium or tin is approximately twice the ratio for the hypothetical compound Mg_2In or the stable compound Mg_2Sn .

Theoretical discussion of the results suggests that aggregates of "small" copper atoms are formed round the "large" atoms of the active elements during solution heat-treatment. Such aggregates would account for the lower rate of natural ageing, if stable at room temperature. Accelerated ageing at elevated temperature could be due to the aggregates acting as nuclei for the formation of Guinier-Preston zones [2]. Alternatively, the aggregates might be capable of rapid rearrangement to Guinier-Preston zones [2] under the influence of thermal fluctuations. A completely different hypothesis of very rapid prior precipitation of the active elements on artificial ageing to form nuclei for Guinier-Preston zones [2] is less satisfactory, as it would not account for the reduced ageing at room temperature.

The results have important practical implications, since they point the way to higher and controlled properties for commercial-purity aluminium-copper alloys.

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I.—INTRODUCTION.

It has recently been shown¹ that tin possesses a slight solid solubility in aluminium. This is of the order of 0.05% at 530° C. and has a very low value at 165° C. Binary aluminium–tin alloys gave a considerable age-hardening effect when artificially aged after solution heat-treatment. The proof-stress values were raised compared with those obtained in the solution heat-treated and naturally aged condition.

It was also found that small additions of tin, of the order of 0.05%, exerted a marked effect on the tensile properties and ageing characteristics of the commercial-purity aluminium–4½% copper (D.T.D. 304 type) alloy. In particular, the alloys containing tin showed considerably enhanced values of proof stress after artificial ageing.

The behaviour of tin in aluminium and aluminium–copper alloys suggested that other elements might be capable of producing similar results and of influencing the course of precipitation of the major solute. Elements closely adjacent to tin in the Periodic Table were chosen for investigation.

At the same time as the experimental work was started, a thorough search was made for previous references to these effects. These were found to be confined almost entirely to the patent literature. The effect of tin on standard aluminium–copper alloys has been described in a series of patents by Nock.² Tin additions of the order of 0.05–0.1% were found to increase the proof stress in the artificially aged condition. A magnesium content of the order of 0.015% was sufficient to militate, in a marked manner, against the effect of the tin addition. It was claimed that this deleterious effect could be overcome by an addition of cadmium to the extent of five times the magnesium content.

II.—SCOPE OF INVESTIGATION.

The work now described forms part of a general investigation of precipitation phenomena in aluminium–copper alloys, and had the following objectives:

- (1) To identify elements exerting a similar effect to tin.¹
- (2) To study their effect on the ageing characteristics of cast and heat-treated aluminium–4% copper alloy made from very high-purity constituents.

Evidence was sought in the first stage of the investigation for the solid solubility in aluminium of the elements closely adjacent to tin in the Periodic Table. The response to artificial ageing of the binary alloys of these elements with aluminium was used to assess their solid solubility. The following elements were examined: cadmium, indium,

tin, and antimony from the Second Long Period; and thallium, lead, and bismuth, from the Third Long Period. Only the first three elements—cadmium, indium, and tin—showed age-hardening in their binary alloys with aluminium and were judged to possess a slight solubility.

The second part of the investigation was concerned with determining which of the elements listed above had any effect on the cast and heat-treated aluminium-4% copper-0.15% titanium alloy. Grain refinement by titanium was employed throughout to ensure greater reproducibility of results. Previous experience had shown that the ageing behaviour was substantially unaffected by the presence of titanium. Tensile properties were obtained on cast and solution heat-treated bars in the naturally and artificially aged conditions.

Additions of cadmium, indium, tin, or bismuth all had some influence on the results of the tensile tests, and in the third part of the work a study was made of the effect of different amounts of these elements. In addition, the comparative precipitation rates and age-hardening response due to additions of cadmium or tin were obtained from ageing curves at 165° and 190° C.

Finally, the effect was investigated of small magnesium additions on the aluminium-4% copper-0.15 titanium alloy containing cadmium, indium, or tin.

III.—EXPERIMENTAL DETAILS.

1. *Preparation of Alloys.*

Super-pure aluminium and materials of the highest available purity were used throughout. Copper, titanium, and magnesium were added in the form of high-purity addition alloys; the other additions were made as the pure materials. Some of the alloys were prepared in alumina crucibles, but others were melted in an H.F. furnace using Salamander crucibles which had been sprayed with a coating of 99% alumina and 1% sodium silicate. Preliminary tests showed that this technique caused no reduction in metal purity. The silicon and iron contents of an aluminium-2% copper alloy which had been prepared under these conditions were 0.003% and 0.001%, respectively. No phases were detected in the aluminium-4% copper-0.15% titanium alloy other than aluminium, CuAl_2 , and TiAl_3 .

The melts were chlorine-degassed through an alumina tube, and all except the binary aluminium alloys were cast as D.T.D. bars in baked sand moulds at 700° C. The binary alloys were water-chill cast by pouring into a cylindrical thin sheet steel container and allowing water in an annular space between this and an outside container to rise at

such a rate that directional solidification occurred from the bottom of the ingot.

2. *Analyses.*

The binary aluminium alloys were analysed only for tin, antimony, or bismuth. The agreement between the nominal and actual values was sufficiently good to encourage the belief that the analyses of the other alloys could be dispensed with. The graphs for the alloys with tin have been plotted against their actual values; nominal figures have been used for the binary cadmium or indium alloys.

Melt analyses of the copper-containing alloys were made in most cases. The copper and titanium values were all satisfactorily close to the nominal figures. The extreme values for copper were -0.14 and $+0.18\%$ from the nominal, but in general the variation was considerably less than this. The majority of the melts were analysed for titanium, which varied from 0.14 to 0.18% . Analyses were always made for tin and cadmium but, owing to analytical difficulties, not for indium. In all cases, the values were close to the nominal figures, and this also applied to the additions of antimony, thallium, lead, bismuth, or magnesium. Allowance has been made for the actual compositions in plotting the graphs except for the alloys containing indium, where nominal values have been used.

3. *Heat-Treatment.*

Duplicate cast bars were solution heat-treated in a circulating-air furnace for 16 hr. at 530°C . and quenched in cold water. The scope of the present investigation did not merit the use of prolonged heat-treatment times to produce complete solution, but the duration was sufficiently long to dissolve all except the remnants of the largest clusters of CuAl_2 particles.

The artificial-ageing treatment normally used was 16 hr. at 165°C ., as experience had shown that this clearly revealed the differences under investigation. Other heat-treatments employed are described below.

IV.—EVIDENCE FOR SOLUBILITY OF Cd, In, Sn, Sb, Tl, Pb, OR Bi IN PURE ALUMINIUM AT 530°C .

1. *Response to Age-Hardening.*

Following the lines of earlier work,¹ the solubilities of the elements concerned have been demonstrated by their response to age-hardening

after solution heat-treatment. Alloys of different concentrations were water-chill cast as $1\frac{1}{4}$ in. dia. billets. The 0.1% proof stress, 0.2% proof stress, maximum stress, and elongation values were determined on duplicate bars solution heat-treated for 16 hr. at 530° C., cold-water

TABLE I.—0.2% Proof Stress Values for Binary Alloys of Aluminium with Elements Indicated.

Duplicate bars solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as shown.

Added Element, wt.-%	0.2% Proof Stress, tons/in. ²			
	Sb	Tl	Pb	Bi
<i>Aged 2-3 weeks at room temperature.</i>				
0.01	0.93
	0.88
0.025	1.05	1.20	1.20	0.92
	1.12	1.12	...	0.95
0.05	1.08	1.06	1.14	0.94
	1.12	1.06	1.14	0.96
0.1	0.99	1.20	1.17	1.12
	0.95	0.92
<i>Aged 16 hr. at 165° C.</i>				
0.01	1.00
	0.99
0.025	0.96	1.08	0.92	0.97
	1.00	0.96
0.05	1.13	0.98	0.98	1.05
	1.04	0.92	1.02	1.09
0.1	1.07	1.02	1.00	1.11
	1.00	0.96	0.92	1.16

quenched, and aged 2-3 weeks at room temperature or for 16 hr. at 165° C.

The 0.2% proof-stress values for the alloys of aluminium with antimony, thallium, lead, or bismuth have been summarized in Table I and show no response to heat-treatment. The absence of precipitation-hardening effects has been taken as evidence of a negligibly small solubility of these elements in aluminium at 530° C.

The values of the 0.2% proof stress for the alloys with cadmium, indium, or tin are shown plotted against composition in Figs. 1-3. Similar curves were given by the 0.1% proof stress. Indium or tin additions appeared to produce greater solution-hardening than cadmium. The marked response to artificial age-hardening indicated a slight

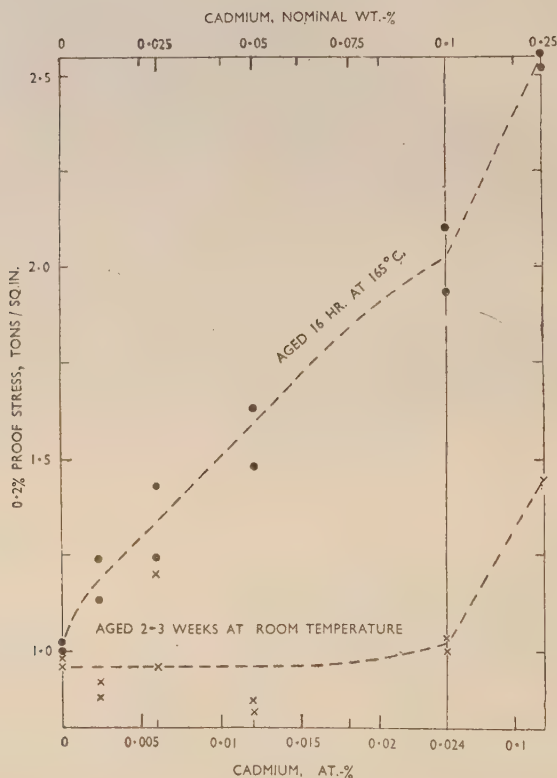


FIG. 1.—0.2% Proof Stress of Aluminium-Cadmium Alloys, water-chill cast, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as indicated.

solubility at 530° C. which was greater than that at 165° C. An indication of the solubility limit at 530° C. may be obtained from the concentration at which the curves for the proof-stress values in the naturally and artificially aged conditions became parallel. This would put the solid solubility of cadmium at about 0.1 wt.-%, and that of tin at

about 0.05 wt.-%. The scatter of results prevented an estimate from being made for the solubility of indium, but it is likely to be of the same order. The response when aged indicates that the solubility at 165° C. is probably considerably below 0.01 wt.-% for all three elements and may well be infinitely small.

It may be noted that the age-hardening of the aluminium-indium alloys occurred at a temperature in excess of the melting point of indium (156.4° C.), when the stable equilibrium phase is a liquid.

2. Discussion of Solubilities.

The solubilities of cadmium, indium, and tin¹ in aluminium have tentatively been estimated as being of the order of 0.05–0.1 wt.-% at 530° C. and negligibly small at 165° C. These values for cadmium are of the same order as those suggested by Hansen and Blumenthal.^{3,4} A figure of approximately 1% at 649° C. was determined from the absence of

a secondary arrest point on the cooling curves. A value of appreciably

less than 0.2% cadmium at 150° C. has been obtained from age-hardening investigations on alloys of different cadmium content.^{4,5} The value of 0.12 wt.-% at 245° C. suggested recently by Dorn, Pietrowsky, and Tietz,⁶ based on lattice-parameter measurements, is greater than would be expected from the present work.

No values have previously been reported for the solubility of indium. The reason for the low solubility and for the miscibility gap in the liquid state is obscure,⁷ since the relative size-factor and valencies are not dissimilar.

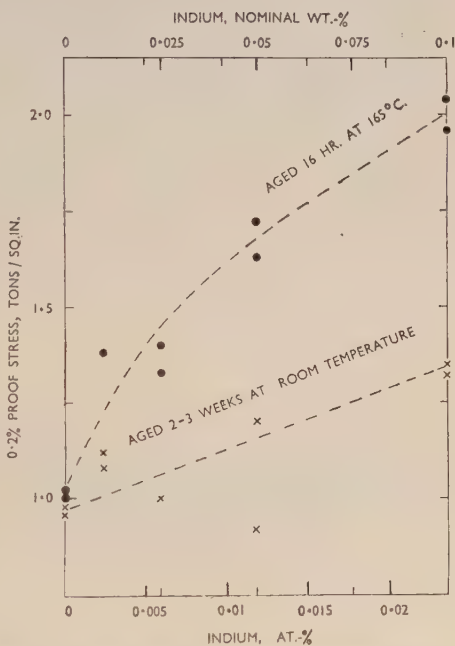


FIG. 2.—0.2% Proof Stress of Aluminium-Indium Alloys, water-chill cast, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as indicated.

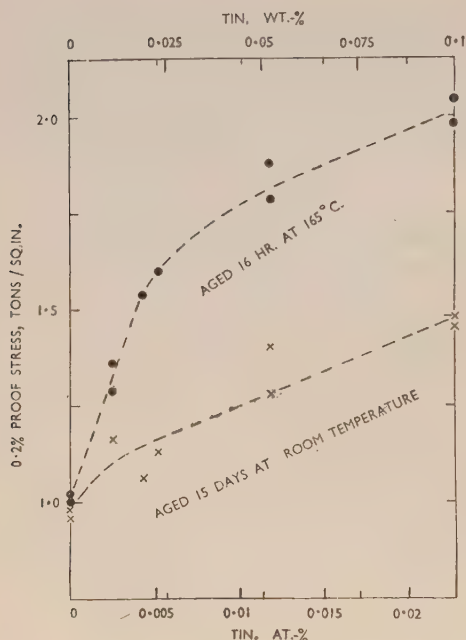


FIG. 3.—0.2% Proof Stress of Aluminium-Tin Alloys, water-chill cast, solution heat-treated 16 hr. at 530° C., and aged as indicated.¹

less than 0.2% at the respective monotectic temperatures of 658.5° C. and 657° C.⁸

V.—EFFECT OF 0.05 WT.-% Cd, In, Sn, Sb, Tl, Pb, OR Bi ON ALUMINIUM-4% COPPER-0.15% TITANIUM ALLOY IN THE NATURALLY AND ARTIFICIALLY AGED CONDITIONS.

The tensile-test results and hardness values are summarized in Table II. It will be seen that additions of antimony, thallium, or lead had no effect on the results obtained on the naturally aged bars. On the other hand, the strength properties after natural ageing, particularly the proof stress, were lowered by additions of cadmium, indium, tin, or bismuth. The effect of the indium or tin additions was most marked.

Cadmium, indium, or tin produced a very considerable increase in the proof stress (almost 100%) and hardness values after artificial ageing. These elements slightly raised the maximum stress and decreased the elongation. Additions of antimony, thallium, lead, or bismuth had no

Both metallographic examination and lattice-parameter measurements were used in the previous work on aluminium-tin alloys and placed the solid solubility close to 0.05% tin at 530° C.¹

The solubilities of antimony, thallium, lead, and bismuth in aluminium have been taken as negligibly small at 530° C. The solubility of antimony has previously been reported as less than 0.1% at the eutectic temperature of 657° C.

No values have been recorded for thallium, but the solubilities of both lead and bismuth have been given as

effect, except that the alloy with bismuth showed a slightly lower maximum-stress value.

The elements antimony, thallium, and lead, which were found to be insoluble in aluminium, had no effect on the response to heat-

TABLE II.—*Effect of Additions of 0.05 wt.-% of Elements Indicated on Tensile Properties and Hardness Values of Aluminium-4% Copper-0.15 Titanium Alloy.*

Averaged results on duplicate sand-cast D.T.D. test-bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as shown.

	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elongation, %	V.P. Hardness Number
Al-4% Cu-0.15% Ti alloy	Aged 14 days at room temperature.			
	10.0	18.1	18	90
Addition Element :				
2nd Long Period				
Group IIb : Cd . .	7.6	16.1	22	89.3
„ IIIb : In . .	4.8	13.9	22½	82.2
„ IVb : Sn . .	4.35	12.8	20	77
„ Vb : Sb . .	9.55	16.5	13½	95.7
3rd Long Period				
Group IIIb : Tl . .	9.8	17.8	17	94.6
„ IVb : Pb . .	10.0	17.3	17	94.7
„ Vb : Bi . .	7.0	16.9	15½	83.5
Al-4% Cu-0.15% Ti alloy	Aged 16 hr. at 165° C.			
	11.9	19.8	10	111
Addition Element :				
2nd Long Period				
Group IIb : Cd . .	21.0	23.5	4½	142
„ IIIb : In . .	22.6 *	23.1	2	144
„ IVb : Sn . .	22.5	23.2	2	135
„ Vb : Sb . .	12.4	18.5	8½	120
3rd Long Period				
Group IIIb : Tl . .	10.6	19.6	11	107
„ IVb : Pb . .	11.3	18.2	9½	109
„ Vb : Bi . .	11.0	17.5	11	113

* 0.05% proof stress.

treatment of the aluminium-4% copper alloy. Bismuth is also insoluble but did have a slight influence on the strength properties.

The soluble elements cadmium, indium, and tin produced a marked effect on the age-hardening response of the aluminium-copper alloy. The strength properties were reduced in the naturally aged condition,

but markedly increased when the alloy was artificially aged. It may be noted that 0.05 wt.-% of these elements is only equivalent to approximately 0.012 at.-%.

VI.—EFFECT OF VARIATION OF CONCENTRATION OF Cd, In, Sn, OR Bi ON ALUMINIUM-4% COPPER-0.15% TITANIUM ALLOY IN THE NATURALLY AND ARTIFICIALLY AGED CONDITIONS.

Cadmium, indium, and tin possess a small but not negligible solu-

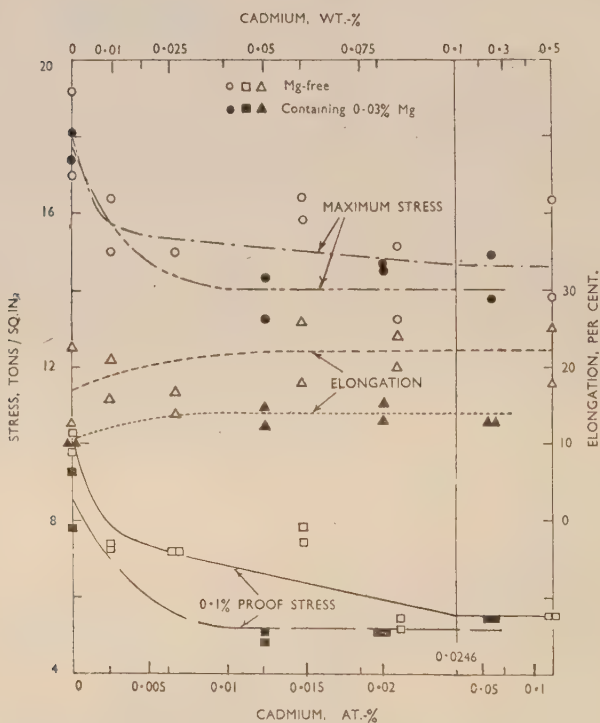


FIG. 4.—Tensile-Test Results on Al-4% Cu-0.15% Ti and Al-4% Cu-0.15% Ti-0.03% Mg Alloys containing various quantities of cadmium. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 14 days at room temp.

bility in aluminium. These elements also exercised the greatest effect on the properties of the aluminium-copper alloy and were selected for further investigation.

As already stated, antimony, thallium, lead, and bismuth are sub-

stantially insoluble in aluminium. This is in agreement with their lack of influence on the ageing of the aluminium-copper alloy except for the apparently anomalous effect of bismuth on the alloy in the naturally aged condition. Only bismuth additions, therefore, were investigated further.

The tensile-test results on the aluminium-4% copper-0.15% titanium

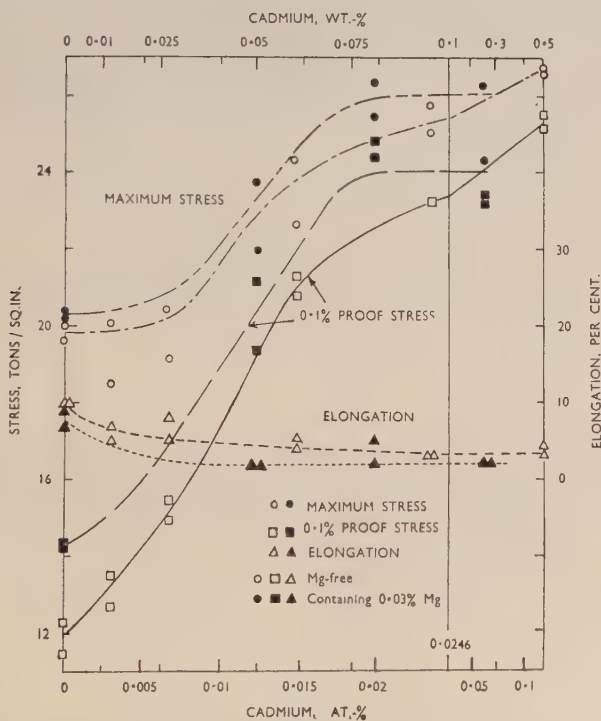


FIG. 5.—Tensile-Test Results on Al-4% Cu-0.15% Ti and Al-4% Cu-0.15% Ti-0.03% Mg Alloys containing various quantities of cadmium. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 16 hr. at 165° C.

alloy containing various quantities of cadmium, indium, tin, or bismuth, after natural ageing for 14 days or artificial ageing for 16 hr. at 165° C., are given in Figs. 4-11. The scatter of the test results made it preferable to draw smooth curves through the experimental points and to ignore minor deviations from the general trends.

The curves for the additions of cadmium, indium, or tin differ only in degree. The naturally aged alloys all exhibited a decrease in their

maximum and proof-stress values (Figs. 4, 6, and 8), whilst the elongation values were slightly raised. Comparison of the graphs shows that tin or indium additions were almost equally efficacious, but that the effects due to cadmium were slightly less pronounced.

The maximum- and proof-stress values were substantially raised with increasing quantities of the three elements when artificially aged

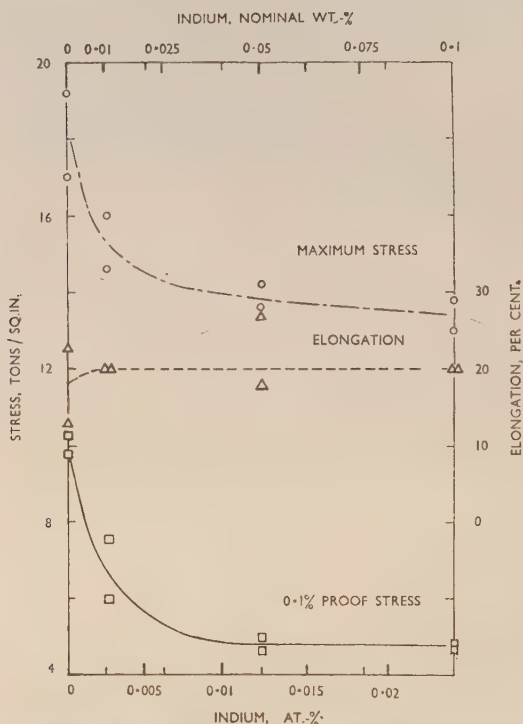


FIG. 6.—Tensile-Test Results on Al-4% Cu-0.15% Ti Alloys containing various nominal quantities of indium. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 14 days at room temp.

(Figs. 5, 7, and 9). The elongation values were reduced, but the increase in the proof-stress values was extremely marked. The comparative effectiveness of the three elements was in the same order as for the naturally aged condition. Tin or indium additions were almost equivalent, cadmium additions were again slightly less effective.

As a result of these tests, it became clear that as little as 0.02 wt.-% (0.005 at.-%) of cadmium, and 0.01 wt.-% (0.0022 at.-%) of indium or

tin, was sufficient to exert a very pronounced influence on the course of precipitation of copper in aluminium.

Additions of 0.05 wt.-% indium and 0.1 wt.-% tin caused the artificially aged test-bars to break before the 0.1% proof stress was reached. This did not occur in the presence of even 0.5 wt.-% of cadmium. The effect is probably associated with the distribution of the excess undissolved cadmium, indium, or tin particles. Spherical

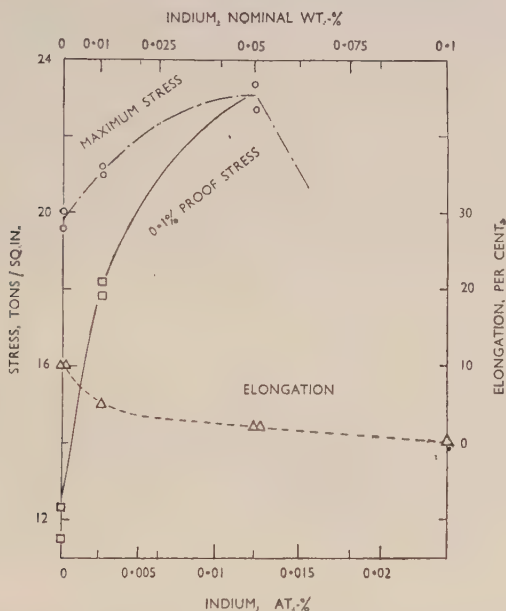


FIG. 7.—Tensile-Test Results on Al-4% Cu-0.15% Ti Alloys containing various nominal quantities of indium. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 16 hr. at 165° C.

globules would have very little influence on the tensile properties, whereas weak, intergranular films would have a serious embrittling action. The relative distribution is bound up with the interfacial tensions of the three elements against aluminium. Ikeuye and Smith⁹ have shown that the interfacial tension cadmium/aluminium is higher than that of tin/aluminium. Undissolved particles of cadmium may be expected to occur more frequently in the form of spheres than undissolved particles of tin. The alloys containing suitable amounts of cadmium showed an equal increase in proof stress, accompanied by the

greatest increase in maximum stress, and lost less ductility than the alloys containing indium or tin.

The effect of bismuth additions is shown in Figs. 10 and 11. The proof- and maximum-stress values were reduced in the naturally aged condition, but the elongation values were unaffected. The maximum-

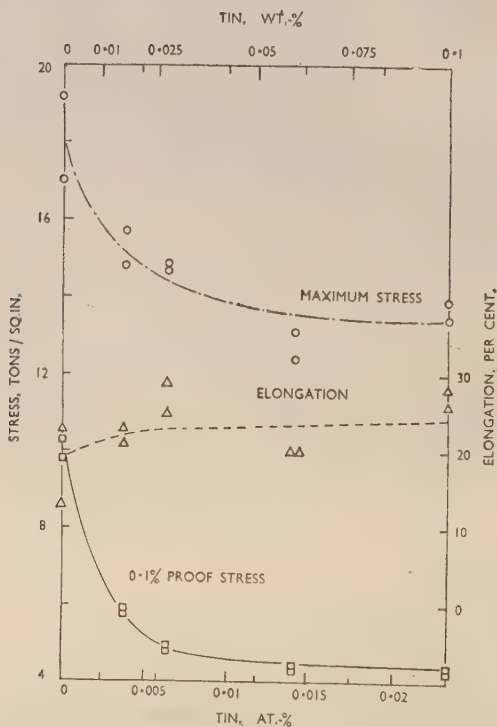


FIG. 8.—Tensile-Test Results on Al-4% Cu-0.15% Ti Alloys containing various quantities of tin. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 14 days at room temp.

stress and elongation values were lower in the artificially aged condition, but the proof stress was unaffected. The effects were largely independent of the bismuth content between the limits investigated above 0.02 wt.-% (0.0025 at.-%). This suggests that the action is entirely a mechanical effect resulting from the presence of undissolved particles. On this view, bismuth has no influence on the course of precipitation of copper in aluminium, although the complete proof of this would require the preparation of ageing curves.

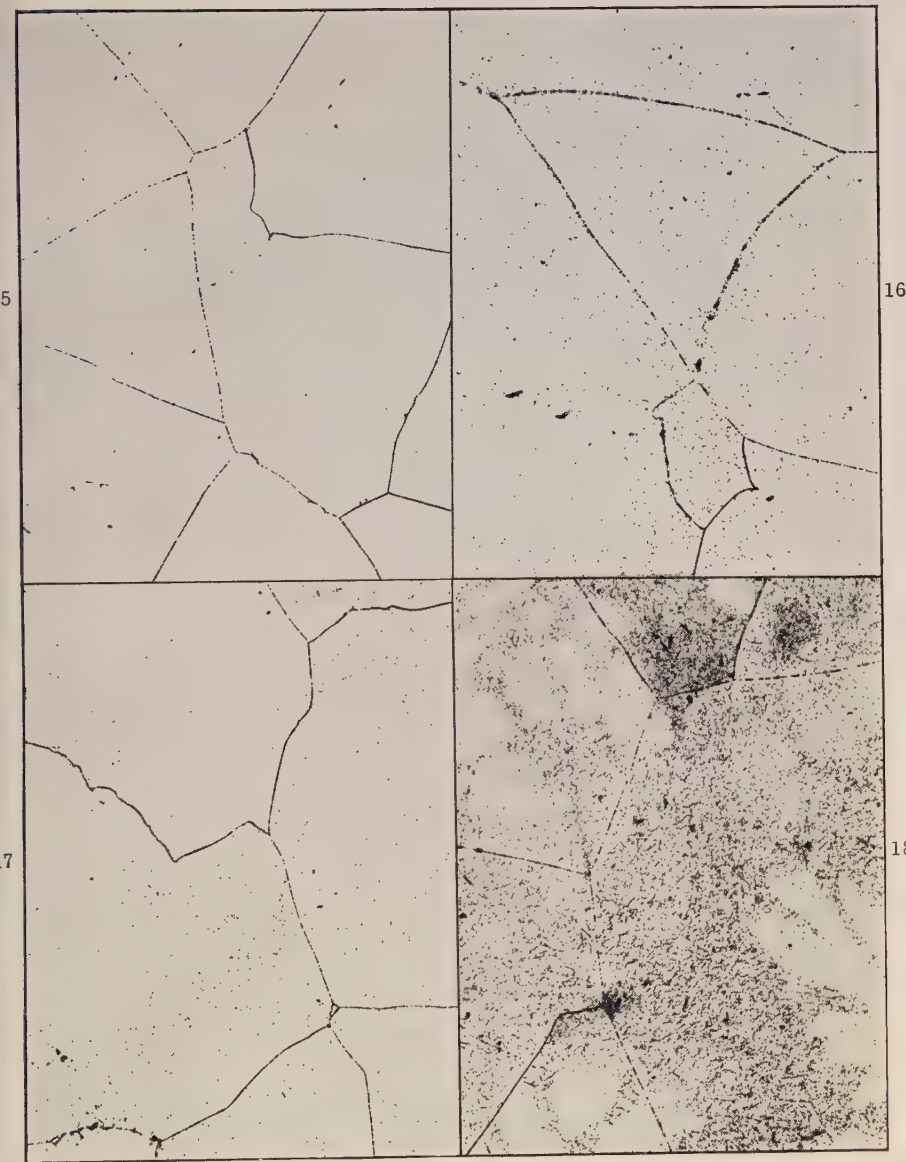


FIG. 15.—Al-4% Cu-0.15% Ti Alloy aged 8 hr. at 190° C.
 FIG. 16.—Al-4% Cu-0.15% Ti Alloy aged 24 hr. at 190° C.
 FIG. 17.—Al-4% Cu-0.15% Ti-0.05% Cd Alloy aged 8 hr. at 190° C.
 FIG. 18.—Al-4% Cu-0.15% Ti-0.05% Cd Alloy aged 24 hr. at 190° C.

All specimens sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched. Etched 3 min. in 25% HNO_3 at 70° C. $\times 250$.

[To face p. 182.]

VII.—THE RATE OF PRECIPITATION AND AGE-HARDENING RESPONSE OF ALUMINIUM-COPPER ALLOYS CONTAINING ADDITIONS OF CADMIUM OR TIN.

The increased strength properties of the artificially aged alloys with cadmium, indium, or tin may be caused by an increase in the rate of precipitation or by an enhanced response to age-hardening, or simul-

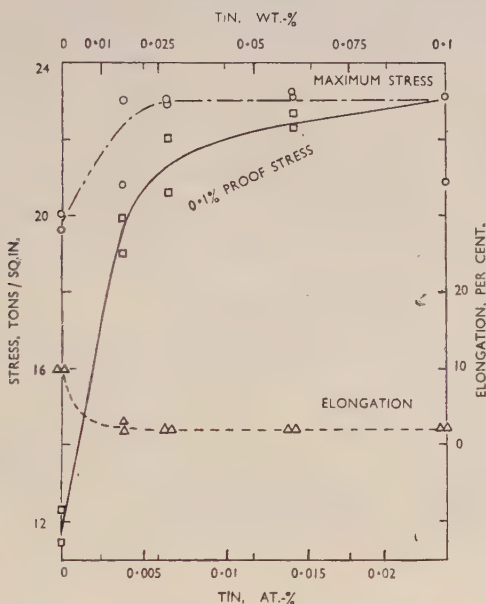


FIG. 9.—Tensile-Test Results on Al-4% Cu-0.15% Ti Alloys containing various quantities of tin. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 16 hr. at 165° C.

taneously by both these factors. This has been examined on the basis of ageing curves at 165° and 190° C.

Tensile-test results on ageing the aluminium-4½% copper-0.15% titanium and the aluminium-4½% copper-0.15% titanium-0.05% cadmium alloys at 165° C. are given in Figs. 12 and 13. The peak proof-stress value, in the absence of cadmium, occurred after about 6 days at 165° C. With an addition of 0.05% cadmium the peak proof stress was reached in about 40 hr.

Fig. 14 shows the hardness/ageing curves at 190° C. for the alumin-

ium-4% copper, aluminium-4% copper-0.01% tin, and aluminium-4% copper-0.05% tin alloys. The tin additions changed the times to maximum hardness from 16 hr. to 4 hr. (0.01% Sn) and to 2 hr. (0.05% Sn). In view of the scatter in results it was considered inadvisable to show a double ageing peak for the aluminium-4% copper alloy.

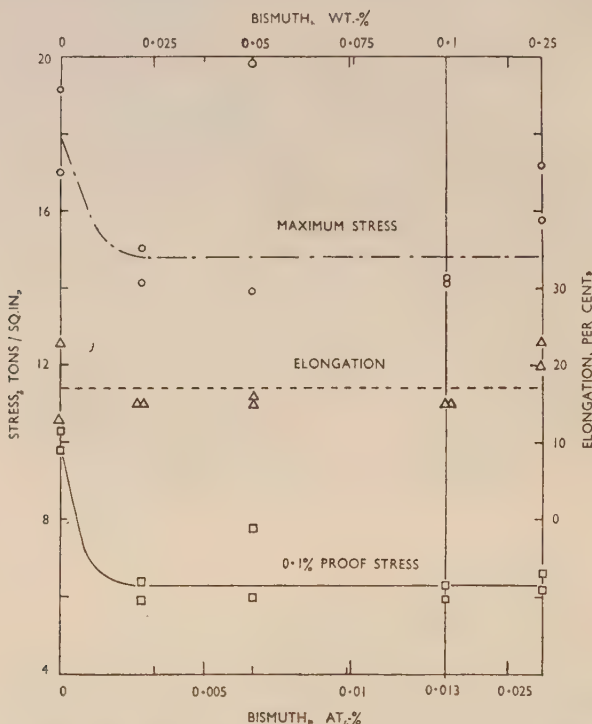


FIG. 10.—Tensile-Test Results on Al-4% Cu-0.15% Ti Alloys containing various quantities of bismuth. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 14 days at room temp.

The presence of these active elements increased the rate of precipitation on artificial ageing by between three and eight times. The age-hardening response has also been enhanced, since both the absolute values and the increment on ageing have been raised considerably. The proof-stress values show this very clearly (see Figs. 12 and 13).

The standard ageing time of 16 hr. at 165° C. is closer to the time to the attainment of maximum properties for the alloys containing the

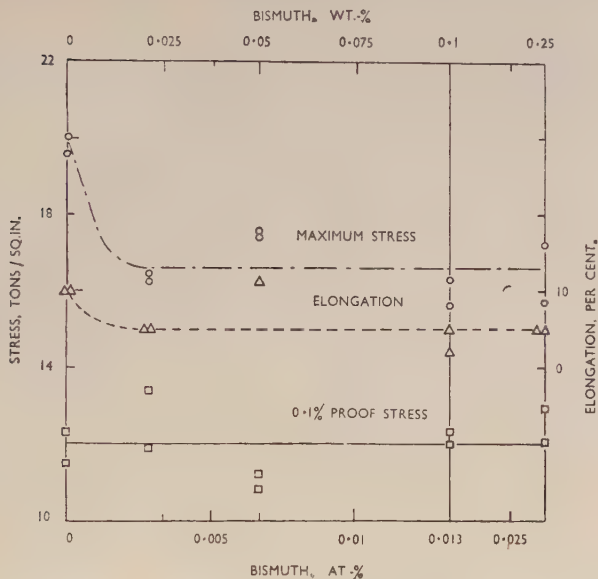


FIG. 11.—Tensile-Test Results on Al-4% Cu-0.15% Ti Alloys containing various quantities of bismuth. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged 16 hr. at 165° C.

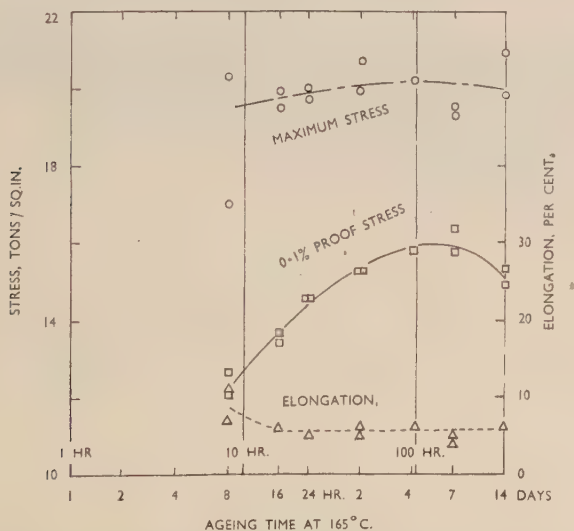


FIG. 12.—Tensile-Test Results on Al-4 1/4% Cu-0.15% Ti Alloys. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged for various times at 165° C.

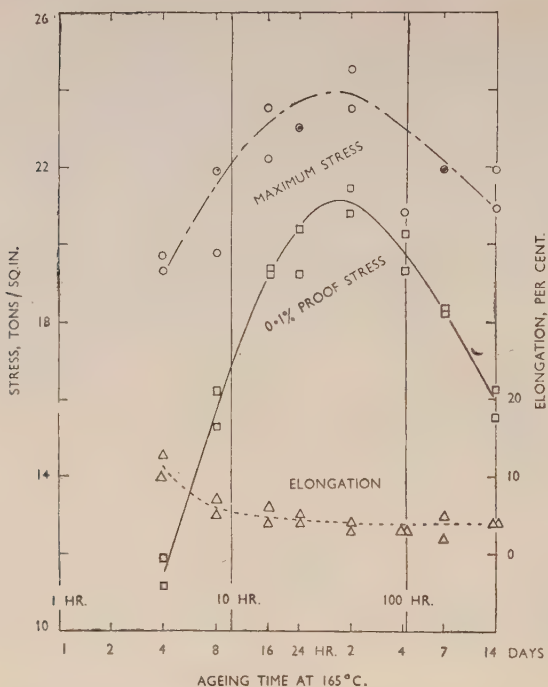


FIG. 13.—Tensile-Test Results on Al-4 $\frac{1}{4}$ % Cu-0.15% Ti-0.05% Cd Alloys. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged for various times at 165° C.

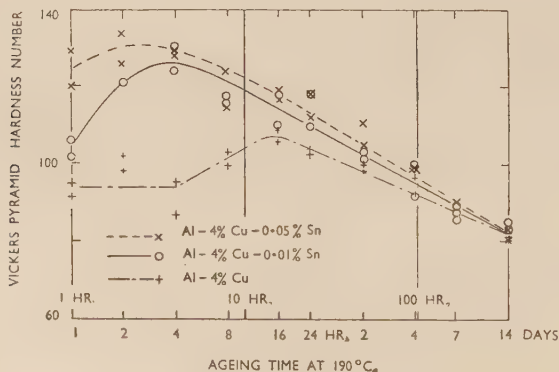


FIG. 14.—Hardness Values on Al-4% Cu, Al-4% Cu-0.01% Sn, and Al-4% Cu-0.05% Sn Alloys. Sand-cast D.T.D. bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged for various times at 190° C.

active elements than for the straight aluminium-4% copper-0.15% titanium alloy. However, the ageing curves show very clearly that the comparisons made on the basis of the standard ageing time are quite valid, because they result from very marked differences in the course of precipitation induced by the presence of cadmium, indium, or tin.

The relative quantities of precipitate were examined metallographically. The structures obtained, when the aluminium-4% copper-0.15% titanium and aluminium-4% copper-0.15% titanium-0.05% cadmium alloys were aged for 8 hr. or 24 hr. at 190° C., are illustrated in Figs. 15-18 (Plate XXX). The cadmium-free alloy showed grain-boundary precipitation after 8 hr. at 190° C. (Fig. 15). At this stage only slight precipitation had occurred within the grains. The alloy containing cadmium (0.012 at.-%) showed slightly more precipitate after 8 hr. than the cadmium-free alloy aged for 24 hr. (Figs. 17 and 16). The cadmium-containing alloy showed extensive precipitation after 24 hr. ageing (Fig. 18) which revealed the original dendritic structure.

VIII.—EFFECT OF SMALL QUANTITIES OF Mg ON ALUMINIUM-4% COPPER-0.15% TITANIUM ALLOY CONTAINING Cd, In, or Sn, IN THE NATURALLY AND ARTIFICIALLY AGED CONDITIONS.

Magnesium forms a strong compound with tin,¹⁰ weak compounds with indium,¹¹ and an uninterrupted solid solution with cadmium.¹⁰ In view of this variation, it was decided to investigate the effect of small quantities of magnesium on the course of precipitation in the presence of the active elements cadmium, indium, or tin. 0.3% tin had no effect on a Duralumin-type alloy containing 0.5% magnesium,¹ and magnesium additions of the order of 0.015% had been reported to militate against the effect of 0.05-0.1% tin on aluminium-copper alloys.²

The effect of magnesium additions of 0.03% or 0.06% on the proof-stress values of the alloys in the naturally and artificially aged conditions is summarized in Table III. The magnesium additions very slightly raised the proof-stress values of the naturally aged alloys containing indium or tin. The cadmium alloys gave rather erratic results in the naturally aged condition.

The proof-stress values of the aluminium-copper alloy containing magnesium were raised when the alloy was artificially aged. The magnesium additions produced very little significant change in the properties of the cadmium-containing alloys. On the other hand, the artificially aged alloys with indium or tin showed a sharp reduction in proof stress (and ultimate stress) with 0.06% magnesium.

The results in Table III show that magnesium had little influence on the alloys containing cadmium. This was confirmed by the similarity between the curves in Figs. 4 or 5 for the cadmium alloys with and with-

TABLE III.—*Effect of Magnesium Additions on 0.1% Proof-Stress Values of Aluminium-4% Copper-0.15% Titanium Alloys with and without Additions of 0.05% Cadmium, Indium, or Tin.*

Averaged results on duplicate bars solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as shown.

Magnesium Addition, %	0.1% Proof Stress, tons/in. ²			
	Al-4% Cu-0.15% Ti Alloy	+ Cd	+ In	+ Sn
<i>Aged 14 days at room temperature.</i>				
nil	10.0	7.6	4.8	4.4
0.03	8.5	4.9	5.3	5.2
0.06	9.5	9.8	6.0	5.1
<i>Aged 16 hr. at 165° C.</i>				
nil	11.9	21.0	22.6	21.4
0.03	14.3	20.4	20.8	20.1
0.06	14.2	20.3	16.3	16.4

out 0.03% magnesium. Small additions of magnesium were without influence on the course of precipitation of copper in aluminium as modified by the presence of cadmium.

The course of precipitation in aluminium-copper alloys containing indium or tin tended to revert to its more normal characteristics with the addition of a small quantity of magnesium. It may be noted that this quantity had to be approximately twice that of the ratio required by Mg_2Sn or Mg_2In before its effect became really appreciable. This is contrary to the previously published findings for alloys containing tin.² Although Mg_2Sn is known to exist close to the aluminium corner of the aluminium-magnesium-tin phase diagram¹, nothing is known of the similar existence of a magnesium-indium compound.

IX.—DISCUSSION OF RESULTS.

1. *Theoretical Considerations.*

It may be accepted that the elements cadmium, indium, and tin owe their influence on the course of precipitation of copper in aluminium

to their solubility in aluminium. There is no reason to believe that this is radically reduced by the presence of copper. That antimony, thallium, and lead have no effect on the precipitation process follows from their negligible solubility in aluminium. The slight influence of bismuth has been attributed to the mechanical effect of the bismuth particles.

Any theory to explain the effect of the active elements must account for the following results :

(i) The rate or extent of natural ageing is depressed.

(ii) Both the rate and extent of artificial ageing are greatly increased.

(iii) The quantity of the active element required is very small.

As little as 0.002 at.-% has an appreciable influence, although about twice this quantity is needed to be really effective.

The possibility that the effects arise from the simple precipitation of the active elements in the aluminium-4% copper alloy, as occurs in their binary alloys with aluminium, may be discounted. This process would hardly bring about the great increases in the response to artificial ageing and, in any case, would not account for the reduced natural ageing of the alloys.

Another possibility is that the presence of the active elements introduces a new phase with ageing characteristics different from those of the aluminium-copper alloys. This might be either a binary phase of the active element with copper, or a ternary phase containing aluminium. None of the active elements forms compounds with aluminium, and the formation of ternary compounds in sufficient quantity to influence the course of precipitation seems unlikely.

It is almost certain that the active elements are capable of influencing the normal precipitation process of copper, as such, in aluminium. Artificial ageing to maximum properties at 165° and 190° C. is believed to be due to the formation of small regions in the parent lattice which are rich in copper and are formed parallel to the (100) planes of the matrix. The distribution of the copper atoms within the group is believed to be random during the initial stages, and this is later superseded by an ordered arrangement which is chiefly responsible for the hardening on ageing at elevated temperatures. The zones of irregular distribution have been designated Guinier-Preston (G.-P.) zones [1] and the ordered regions G.-P. zones [2].¹²

The active elements could influence the rate of precipitation by affecting the rate of diffusion of copper or the rate of nucleation of the G.-P. zones. It would be hazardous to guess at their influence on the rate of diffusion, but the rate of nucleation could be affected in two ways.

The individual atoms of the active element might act as nuclei about which the G.-P. zones could form rapidly. This process is ruled out because it would not be expected to decrease the rate of natural ageing. It is possible that the active elements are themselves precipitated rapidly on artificial ageing. If these particles of precipitate possessed a suitable lattice spacing they could act as nuclei on which the ordered copper regions, the G.-P. zones [2], could be formed. There is insufficient knowledge of the kinetics of precipitation of copper or the active elements in aluminium to decide whether this process could lead to an acceleration of the right order of magnitude, i.e. about five times. The three active elements are very similar in their effectiveness and their precipitation products would require very similar lattice spacings if they were each to act as nuclei for the G.-P. zones [2]. This is not unlikely, since their first-formed precipitate is probably coherent with the aluminium lattice. That this is so is suggested by their age-hardening effects, and particularly since binary aluminium-indium alloys show this effect at a temperature in excess of the melting point of indium. The hypothesis of prior precipitation does not, of itself, explain the reduced natural-ageing capacity, and this would require an additional hypothesis such that the rate of diffusion was lowered by the presence of the active elements. The hypothesis of prior precipitation cannot be discarded immediately, but the experimental finding of reduced natural ageing militates strongly against it.

One view of the manner in which the copper atoms and active atoms interact in aluminium may be based on a consideration of their atomic size in relation to the size of the aluminium atoms. If the closest distance of approach is taken as a measure of the size of the atom,¹³ it is clear that copper has atoms smaller than those of aluminium, whilst those of cadmium, indium, or tin are larger. Copper decreases the lattice spacing of aluminium,⁷ and it is reasonable to suppose that the active elements would increase it. Experimental evidence is available suggesting that tin has this effect,¹ Hansen and Blumenthal³ found that cadmium expanded the aluminium lattice, although Dorn, Pietrokowsky, and Tietz have recently reported a contraction.⁶ No information is available on the behaviour due to indium. The very low solubility of the active elements indicates a high interaction energy with the aluminium atoms forming the lattice, and this may effectively alter their apparent size in solution from that deducible from the pure elements. The evidence is by no means decisive, but it will be assumed in the following discussion that the atoms of the active elements are larger than the aluminium atoms.

This relationship could give rise to a preferred distribution of copper

atoms during solution heat-treatment leading to their segregation about the atoms of the active elements. By this means the lattice strain energy associated with each atom separately would be mutually reduced. The aggregation of the "small" copper atoms around the "large" atoms of the active elements would be expected to diminish the overall strain energy of the solid solution (Fig. 19). This hypothesis is analogous to the manner in which Cottrell¹⁴ has postulated that solute atoms can reduce the strain energy associated with a dislocation. Electronic energy interactions between copper and the active elements may also play a part, possibly a dominant part, in this process. For simplicity, however, the effects visualized have been described in terms of atom "sizes".

These aggregates of copper atoms might well be sufficiently stable,

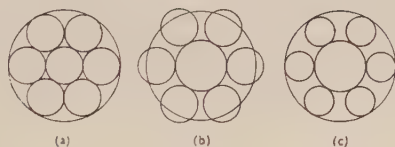


FIG. 19 (a), (b), and (c).—Diagrammatic representation of manner in which a group of small atoms may reduce the lattice strain energy associated with a large atom.

(a) A group of atoms in the parent lattice.

(b) Expansion of this group due to the introduction of a larger atom.

(c) Reduction in volume of the aggregate due to the presence of smaller atoms surrounding the larger atoms.

when quenched to room temperature, to account for the reduced natural ageing capacity in the presence of the active elements.

Accelerated ageing at elevated temperature could arise in two ways. It is possible that the aggregate of copper atoms around the atoms of the active elements could act as nuclei for the formation of G.-P. zones [2]. An alternative view is that ageing at elevated temperatures would give rise to energy fluctuations sufficiently large to allow rearrangement of the aggregates so that the copper atoms would then be able to take part in the precipitation process. It would be idle to speculate on the details of this change, as so many possibilities exist which can only be clarified by further experimental work. The exact mechanism may be neglected at this stage, but the structure visualized is such that groups of copper atoms are already present and are very favourably placed for the formation of G.-P. zones [2].

In the absence of detailed experimental work, it is not possible to

explain in detail the enhanced artificial ageing capacity of the alloys. It may be due either to an increase in the number of particles of precipitate or to an increase in their size for a given ageing time. The former effect has been shown experimentally, but both factors may operate simultaneously.

Although the quantity of the active elements required is very small, 0.005 at.-% (0.02 wt.-%) would give rise to one atom every 27 atomic distances if evenly distributed in the aluminium-4% copper (1.74 at.-%) alloy. This is of the same order as the distance between the particles of precipitate formed when the aluminium-4% copper alloy is aged at room temperature. These are thought to be about 50 atom spacings distant from one another.¹⁵

The experimental observations can be accounted for on the basis of short-range grouping of copper atoms around the active atoms during solution heat-treatment. Indium or tin atoms are equally effective, cadmium somewhat less so. This may be due to the cadmium atom being slightly smaller than that of indium or tin.

Magnesium additions diminished the effect of indium or tin, but were without influence on the alloys containing cadmium. This can be explained on the basis of the tendency of these elements to form compounds with magnesium. The binary equilibrium diagrams suggest that this tendency is very strong, weak to medium, and very weak, for tin, indium, and cadmium, respectively. The quantity of magnesium required to suppress the effect of indium or tin is approximately twice the ratio for the hypothetical compound Mg_2In or for the stable compound Mg_2Sn . It is not known whether magnesium atoms remove indium or tin from the solid solution to form insoluble binary compounds. An alternative view is that the magnesium atoms will replace preferentially the copper atoms in the atmosphere around the tin or indium atoms in the aluminium solid solution. Although the magnesium atoms are also larger than aluminium atoms, the electrochemical effects may be sufficiently strong to over-rule the simple strain-energy size effect suggested for the interaction of the copper atoms with the atoms of indium or tin.

The prior-precipitation theory would explain the effect of magnesium by assuming that the precipitate first formed was based on a magnesium-indium or magnesium-tin compound. The lattice spacing of the precipitate would no longer be similar to that of the G.-P. zones [2], so that no nucleation would be expected, though the absence of a strong magnesium-indium compound militates against this view.

The experimental evidence available at the moment favours the hypothesis of short-range grouping of the copper atoms around the

active elements during solution heat-treatment. The decreased capacity for natural ageing militates against the hypothesis of prior precipitation of the active elements. However, only further experimental work will decide finally between the alternative hypotheses which have been described, and a detailed examination is being made of the ageing process in these alloys.

2. Practical Implications.

The variable response to heat-treatment of the cast aluminium-4½% copper alloy, which is sometimes experienced, may well be due to the chance occurrence of small quantities of cadmium, indium, or tin. These elements are not normally sought by analysis in the quantities necessary to cause the effects described above. The aluminium-4½% copper alloy is not, of itself, capable of giving the mechanical properties expected by D.T.D. 361, unless additions of the elements such as cadmium, indium, or tin are present in the amounts desired.

Small quantities of cadmium, indium, or tin could be used to give enhanced proof- and maximum-stress values in artificially aged aluminium-copper alloys. The slower rate of natural ageing may also be of practical value in allowing fabricating processes to be carried out between solution heat-treatment and artificial ageing. Cadmium is probably the most useful element for this purpose, as the quantity required is less critical than that of indium and tin and the ductility is reduced to a smaller extent. Furthermore, cadmium additions are not neutralized by the presence of small quantities of magnesium.

ACKNOWLEDGEMENTS.

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THE ALLOTROPY OF MANGANESE.*

1276

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SYNOPSIS.

Free energy/temperature relations are calculated for the α , β , and γ forms of manganese, using existing thermodynamic data. In the case of the α and γ forms, relative free-energy curves can be drawn over the whole temperature range from 0° to 1400° K., the free energies being expressed in terms of the heat content of the α phase at the absolute zero. The difference in internal energy of these two forms at 0° K. is 342 cal./g.-atom. For the β phase a free-energy curve can be constructed for the temperature range 300° – 1400° K. in terms of the heat content of the β phase at room temperature. This is related to the α and γ phases by making $G^\beta = G^\gamma$ at the $\beta \rightleftharpoons \gamma$ transformation temperature, and it is then found that the difference in free energies of the α and β phases at the $\alpha \rightleftharpoons \beta$ transformation temperature is only 5 cal./g.-atom, i.e. the results are self-consistent. The results for the γ phase are obtained on the assumption that electrolytic γ -manganese has the same structure as the high-temperature form.

I.—INTRODUCTION.

MANGANESE is known to exist in three different crystallographic modifications, the α , β , and γ forms, each of which is stable over a certain temperature range. It now appears fairly certain that a fourth form, δ -manganese, constitutes the equilibrium structure at temperatures immediately below the freezing point, but it has not yet been possible to determine its crystal structure. The properties of manganese, which occurs midway in the First Long Period of the Periodic Table, are very different from those of the two neighbouring elements iron and chromium, and for this reason it is of great theoretical interest. Any satisfactory theory of the transition elements will have to explain the relatively low melting point and the occurrence of the complicated, brittle α and β structures. In this paper free energy/temperature relations for the α , β , and γ forms are derived from existing thermodynamic data.

The α form of manganese is stable up to about 700° C., the exact transformation temperature being unknown because of the very large temperature hysteresis accompanying the $\alpha \rightleftharpoons \beta$ change. Methods based on the solubility of hydrogen in manganese¹ and on the heat content of manganese at high temperatures² both give a transformation temperature of 727° C. (1000° K.). α -Manganese has a complex cubic

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structure with a body-centred unit cell of side 8.894 kX., containing 58 atoms.³ The β -manganese structure, which can be retained in pure manganese by quenching, also has a cubic structure, with 20 atoms in the unit cell.⁴ It is stable up to 1100° C., at which temperature the $\beta \rightleftharpoons \gamma$ transformation occurs. The further transformation $\gamma \rightleftharpoons \delta$ takes place at 1138° C. All these transformation temperatures are taken from the paper by Potter and Lukens,¹ who summarized recent determinations and gave a table of most probable values.

Pure γ -manganese cannot be retained by quenching, a certain amount of transformation into β or α always occurring. It is usually assumed that γ -manganese has a face-centred tetragonal structure with $a = 3.774$ kX. and $c/a = 0.93$. The evidence for this is based on the parameters of some manganese-rich alloys in which the γ phase can be retained by quenching, and also on the fact that when manganese is electrodeposited under certain conditions a face-centred tetragonal structure, which slowly transforms to α -manganese at room temperature and is assumed to be identical with the γ form, is obtained. In most alloy systems where appreciable solid solution is found in the γ phase, the structure changes gradually to face-centred-cubic through a progressive alteration of the axial ratio. The highly-twinned structure of some quenched copper-manganese alloys⁵ has led Zener⁶ to suggest that γ -manganese is itself face-centred cubic and that it transforms to face-centred tetragonal by a shear process during quenching. The electrodeposited face-centred tetragonal structure need not, of course, be the same as the high-temperature γ form—many examples are known of metastable electrodeposited structures which do not correspond to the equilibrium structure at any temperature. The thermodynamic data discussed in this paper, however, indicate that the γ phase is the same as that obtained by electrodeposition.

II.—SPECIFIC-HEAT AND HEAT-CONTENT MEASUREMENTS.

Shomate⁷ has measured the low-temperature specific heats of both the α and the (electrodeposited) γ forms of manganese, and from the results obtained he was able to plot a specific-heat curve from 52° to 298.16° K. The γ phase was prepared by electrodeposition followed by immediate cooling to the temperature of solid carbon dioxide. For both forms the measurements below 100° K. could be fitted to a single Debye function (excluding a small specific-heat anomaly in the α curve) and the curves were thus extrapolated down to 0° K.

The specific heat of manganese between 16° and 22° K. has been measured by Elson, Grayson-Smith, and Wilhelm,⁸ who found the specific heat in this range to be given by a sum of a linear term $0.00421 T$

and a Debye term with characteristic temperature 410° K., which differs considerably from the characteristic temperature 348° K. obtained by Shomate. The method used in the low-temperature measurements seems reasonably accurate, but no information is given about the purity of the manganese. As manganese lies in the middle of the First Transition Period of the Periodic Table, it is to be expected that the electronic contribution to the specific heat will be comparatively large and will be important at very low and very high temperatures. The results of Elson, Grayson-Smith, and Wilhelm are in agreement with this, and Shomate was probably not justified in using a single Debye function for the results below 50° K. The specific heat at 54.2° K., calculated from the low-temperature equation, is 1.180 cal./g.-atom, compared with 1.380 cal./g.-atom found experimentally by Shomate.* In general, however, Shomate's results may be regarded as reliable and, as the heat contents and entropies up to 54° K. are small compared with the heat contents and entropies at 298.16° K., it has been considered quite justifiable to use his values in the present paper.

Naylor² measured the heat contents of manganese in the region 298.16° – 1450° K. by the "drop" method, and obtained for each temperature of observation the differences between the heat content and entropy of the sample at that temperature and the heat content and entropy of α manganese at 298.16° K. Recently, Armstrong and Grayson-Smith⁹ have determined the specific heat of manganese in the range 0° – 800° C. by a direct method using an adiabatic calorimeter.

From the results of these papers relative free energy/temperature curves can be constructed from 0° to 1400° K. for the α and γ phases, and from 298.16° to 1400° K. for the β phase, provided that certain extrapolations are made.

At any given temperature the most stable structure will be that for which the Gibbs' function :

$$G = H - TS$$

(where H is the heat content and S the entropy) has a minimum value. At a temperature T the value of H for a particular phase is given in terms of the value H_0 at the absolute zero by :

$$H_T - H_0 = \int_0^T C_p \cdot dT,$$

while the value of S is given by :

$$S_T = \int_0^T \frac{C_p}{T} \cdot dT.$$

* Strictly, the Debye function gives C_v , but at low temperatures the difference $C_p - C_v$ is negligible.

Values for G have been calculated in terms of H_0^a , the heat content of the α phase at the absolute zero.

From Shomate's data we have :

$$\begin{aligned}H_{298.16}^a - H_0^a &= 1193 \text{ cal./g.-atom} \\S_{298.16}^a &= 7.59 \text{ E.U./g.-atom} \\H_{298.16}^\gamma - H_0^\gamma &= 1221 \text{ cal./g.-atom} \\S_{298.16}^\gamma &= 7.72 \text{ E.U./g.-atom}\end{aligned}$$

Naylor's heat-content results give values of $H_T^a - H_{298.16}^a$ and $S_T^a - S_{298.16}^a$ for temperatures from 298.16° to 1000° K., and hence G^a values for the α phase in this range are readily obtained in terms of H_0^a . G^a values can also be derived from Armstrong and Grayson-Smith's results, either by graphical integration of their specific-heat curve, or by numerical integration of an empirical curve chosen to represent the results as closely as possible.

From his results Naylor obtained the following equation for the specific heat of the α phase at temperatures up to 1000° K. :

$$C_p^a = 5.70 + 0.00338T - 37,500/T^2.$$

Values calculated from this equation agree reasonably well with the direct results for the specific heat, the maximum deviation being within 3%. The direct determinations of specific heat are, of course, much more accurate, since the heat-content measurements give the mean specific heat over a temperature range as the difference between two large quantities, and the experimental difficulties are also greater. On the other hand, the heat-content results obtained from integration of Armstrong and Grayson-Smith's curve will not be very much more accurate than the direct measurements of heat content made by Naylor.

The results for the direct specific-heat curve are such that it cannot be fitted exactly to an equation of the type $C_p = A + BT + C/T^2$. The best agreement is obtained from the equation :

$$C_p = 5.43 + 0.00343T - 20,000/T^2$$

which gives a mean deviation of 0.36% over the smooth-curve values from 0° to 700° C. The deviation at 700° C., however, is much larger (1.5%) than at any other temperature and, as it is desirable to extrapolate the curve to higher temperatures, this is a disadvantage. For this reason, and also so that the comparison of G^a values with G^β and G^γ values may be more consistent, Naylor's C_p equation has been used for the calculation of G^a values up to 1400° K. Calculations from Armstrong and Grayson-Smith's results give values for H^a and S^a which are both a little lower than those obtained from Naylor's equation, and the

corresponding G^{α} values are slightly higher, though the difference is everywhere less than 1%.

For the γ phase Naylor's values give $H_T^{\gamma} - H_{298.16}^{\alpha}$ and $S_T^{\gamma} - S_{298.16}^{\alpha}$. Using these results and Shomate's values for $(C_p^{\gamma})_{298.16}$ and $(\frac{\partial C_p^{\gamma}}{\partial T})_{298.16}$ he obtained the equation :

$$C_p^{\gamma} = 6.03 + 0.00356T - 44,300/T^2$$

for the specific heat in the range 298.16° to 1400° K. G^{γ} values can thus be obtained in terms of H_0^{γ} . These values are obtained in terms of H_0^{α} using the relation :

$$(H_T^{\gamma} - H_0^{\gamma}) + H_0^{\gamma} = (H_T^{\gamma} - H_0^{\alpha}) + H_0^{\alpha}$$

giving $H_0^{\gamma} - H_0^{\alpha}$.

The atomic heat of β -manganese at 1000° K. was found to be 8.96 cal./ $^{\circ}$ C. by Armstrong and Grayson-Smith, in very good agreement with the value 8.99 cal./ $^{\circ}$ C. obtained by Naylor. The direct determinations do not provide sufficient data for the construction of an extrapolated specific-heat curve, and Naylor's values have therefore been used. It is necessary to extrapolate his specific-heat curve over a wide temperature range to obtain G^{β} values, and this procedure is open to objection. The agreement of the values at 1000° K. suggests that Naylor's results are not affected by the $\alpha \rightleftharpoons \beta$ transformation to any appreciable extent, but a slight error here would lead to considerable errors in the extrapolated curve.

No low-temperature specific-heat data are available for β -manganese, but it is possible that, as the pure β phase can be retained by quenching, such values could be obtained and more accurate free-energy values calculated. From the high-temperature heat-content work on β -manganese, Naylor found that a specific heat equation :

$$C_p^{\beta} = 8.33 + 0.00066T$$

fitted his results from 1000° to 1374° K. with a mean deviation of 0.2%. This equation has been assumed to be valid for the temperature range 298.16° – 1000° K., and values have been calculated from it of $H_T^{\beta} - H_{298.16}^{\beta}$ and $S_T^{\beta} - S_{298.16}^{\beta}$. Using the relation :

$$(S_T^{\beta} - S_{298.16}^{\beta}) + S_{298.16}^{\beta} = (S_T^{\beta} - S_{298.16}^{\alpha}) + S_{298.16}^{\alpha}$$

$S_{298.16}^{\beta}$ is found to be 6.68 E.U./g.-atom. Values of G^{β} can therefore be found in the range 298.16° – 1400° K. in terms of $H_{298.16}^{\beta}$. As no information on low-temperature specific heats is available, it is clearly not possible to get G^{β} in terms of H_0^{β} and to compare H_0^{β} with H_0^{α} , as was done for the γ phase. For both the α and γ structures a considerable deviation from the Debye forms occurs above 100° K., so that it is not justifiable to use a single Debye curve for the β -manganese specific heat.

The procedure adopted to relate $H_{298.16}^{\beta}$ to H_0^{α} is to fit the G values at a transformation temperature. At the $\alpha \rightleftharpoons \beta$ transformation $G^{\alpha} = G^{\beta}$, and at the $\beta \rightleftharpoons \gamma$ transformation $G^{\beta} = G^{\gamma}$.

As the $\beta \rightleftharpoons \gamma$ transformation temperature is known more accurately than the $\alpha \rightleftharpoons \beta$ temperature, G^{β} has been made equal to G^{γ} at 1374° K. The results are then self-consistent and the extrapolations justified if $G^{\beta} = G^{\alpha}$ at the $\alpha \rightleftharpoons \beta$ transformation temperature.

III.—RESULTS FOR FREE ENERGIES.

Table I shows the results for G_T for the three phases, the results for β having been adjusted to make $G^{\beta} = G^{\gamma}$ at 1374° K. It will be seen

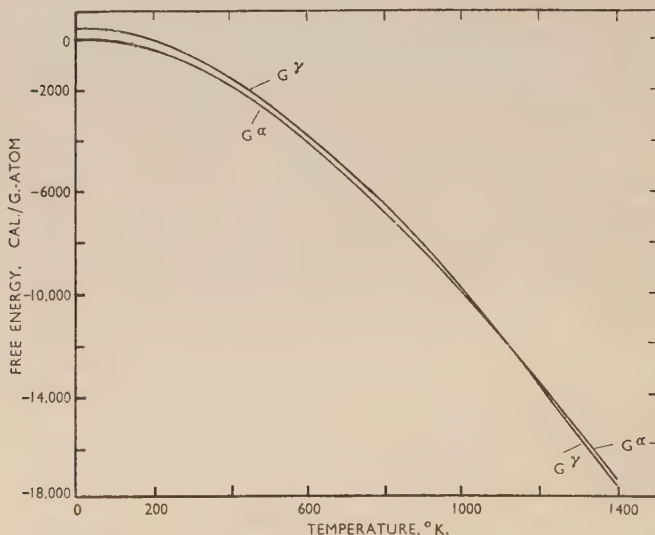


FIG. 1.—Relation between Free Energy and Temperature for α - and γ -Manganese.

that $G^{\beta} - G^{\alpha}$ is only 5 cal./g.-atom at 1000° K., i.e. the results give the correct temperature for the $\alpha \rightleftharpoons \beta$ transformation. The differences in free energy between the three phases are everywhere very small, as an examination of Table I will reveal. In Fig. 1 the free energies for the α and γ phases are plotted against temperature and the curves are so close as to be almost indistinguishable on the scale used. Fig. 2 shows the free energies of the β and γ phases with respect to the α phase as a standard. It is not clear whether the curve for $G^{\beta} - G^{\alpha}$ is becoming incorrect near 298.16° K. because of unjustifiable extrapolation of the specific-heat equation (see above) or whether the fall in $G^{\beta} - G^{\alpha}$ there is a genuine effect.

The results show that at the absolute zero of temperature $H_0^\gamma - H_0^\alpha = 342$ cal./g.-atom, and this is the difference in the internal energies of the phases at 0° K. At room temperature $G^\beta - G^\alpha = 109$ cal./g.-atom and $G^\gamma - G^\alpha = 331$ cal./g.-atom.

TABLE I.— G_T Values for α -, β -, and γ -Manganese.

$T, ^\circ\text{K.}$	G^α , cal./g.-atom	G^β , cal./g.-atom	G^γ , cal./g.-atom
0	0	...	+ 342
298.16	— 1,070	— 961	— 739
400	— 1,949	— 1,777	— 1,636
500	— 2,987	— 2,794	— 2,692
600	— 4,169	— 3,987	— 3,898
700	— 5,474	— 5,331	— 5,250
800	— 6,892	— 6,791	— 6,614
900	— 8,421	— 8,370	— 8,292
1000	— 10,047	— 10,042	— 9,977
1100	— 11,738	— 11,808	— 11,759
1200	— 13,553	— 13,667	— 13,627
1300	— 15,421	— 15,588	— 15,566
1374	— 16,859	— 17,058	— 17,058
1400	— 17,365	— 17,579	— 17,601

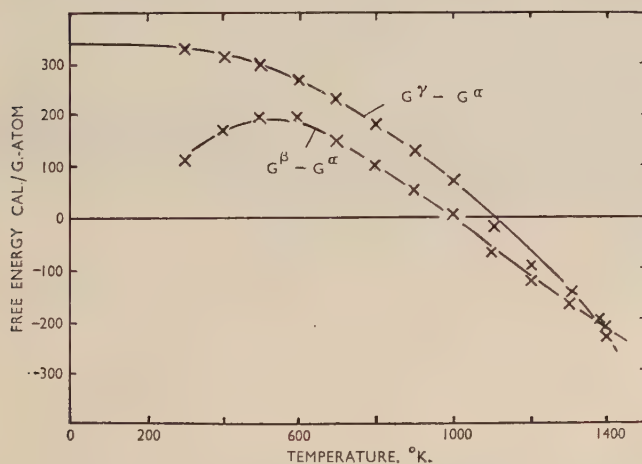


FIG. 2.—Relation between Free Energy and Temperature for β - and γ -Manganese with Respect to α Phase as Standard.

IV.—THE STRUCTURE OF γ -MANGANESE.

The results for γ -manganese given above rest on the assumption that the electrodeposited face-centred tetragonal structure is the same as the high-temperature γ structure. In so far as the results are self-consistent and give free-energy curves of the expected shape, they can be taken as

indicating that this assumption is justified. The only conclusive evidence, however, would be a high-temperature X-ray photograph of γ -manganese, and for practical reasons this is very difficult to obtain.

The transformation from electrolytic γ -manganese to α -manganese at temperatures from 0° to 100° C. has recently been investigated by Potter, Lukens, and Huber,¹⁰ using X-ray and electrical-resistivity measurements. On plotting resistivity against time they obtained a typical S-shaped curve showing slow initial and final transformation rates. X-ray evidence indicated that β -manganese was not formed. The free-energy results given above show that G^β is intermediate between G^α and G^γ , and hence nuclei of α must form and grow from γ at least as readily as nuclei of β . When a metastable phase transforms, the first product of the transformation is not the arrangement with the lowest free energy but is that structure, having a lower free energy than the metastable state, which forms at the greatest rate under the specified conditions. In many cases a phase having a free energy intermediate between the initial and final free energies is first formed, and this accounts for the existence of many metastable transformation products. The decomposition of γ -manganese below the $\alpha \rightleftharpoons \beta$ transformation does not apparently involve an intermediate product. In many manganese-rich alloys where the γ phase transforms on quenching the resultant structure is that of α -manganese and not, as might be expected, β -manganese.

δ -Manganese transforms completely on quenching in pure manganese and in all known alloy systems, so that its crystal structure is unknown. The high-temperature heat-content data are insufficiently sensitive for an approximate free-energy curve to be calculated.

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STRESS-AGEING TREATMENT AND ITS EFFECTS ON THE PHYSICAL PROPERTIES OF COPPER-, IRON-, AND ALUMINIUM-BASE ALLOYS.*

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SYNOPSIS.

"Stress-ageing" is a treatment which consists of heating an alloy, for the correct time and at a suitable temperature, while it is subjected to a specific stress from an external load. By this treatment it is possible, in alloys that possess recrystallization temperatures effectively above room temperature, to double and almost treble the elastic properties, to increase the tensile strength, and simultaneously to raise the elongation and electrical conductivity. These effects may at present be explained within the framework of the Phase Rule by supposing strain-induced solid-state reactions to take place within elastic solid-solution crystal lattices.

More economical use of alloys, replacement of higher-cost alloys by previously inferior materials, and some saving of certain strategic metals, may prove possible by the employment of stress-ageing. The incidental occurrence of this phenomenon during engineering service of alloy parts may prove to be a major factor in fatigue, in second-stage creep, &c. The detailed effects of this treatment on the properties of eight copper-base, five iron-base, and eleven aluminium-base alloys are presented.

I.—INTRODUCTION.

"STRESS-AGEING" is a new treatment consisting of heating alloys, composed wholly or in major part of a solid-solution phase (or phases), for correct times at suitable temperatures while the material is subjected to stress from an external load. By means of this new treatment, it is possible in certain alloys to produce remarkable improvements in the mechanical properties and also in many cases in the electrical conductivity.

The most effective stresses are those ranging from the proportional limit to the 0.2% yield strength of the alloy in its previously prepared condition (i.e. as annealed, as cold worked, or as heat-treated). Since, in almost all instances, the proportional limit is below the elastic limit, such a stress will usually not result in any material creep for periods of from 4 to 20 hr. In many cases, stresses as high as the 0.2% offset yield strength are so close to the elastic limit that the creep resulting from

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such a stress during a period of 4-20 hr. is either immeasurably small or negligible as regards any effect on dimensions. The effective temperatures for stress-ageing are those within the range from room temperature to the recrystallization temperature of the alloy concerned. Above the recrystallization temperature, the annealing (or re-solution) reaction exceeds the stress-ageing reaction, and creep under such high stresses is very rapid and completely damaging.

II.—TREATMENT AND TEST METHODS.

The samples that were treated and tested to demonstrate stress-ageing consisted of standard tensile bars, about $4\frac{3}{4}$ in. long, with threaded ends of $\frac{3}{4}$ in. dia., and a central reduced section about $2\frac{1}{2}$ in. long. The diameter of the central reduced section varied for different alloys: from 0.505 in. for lower-strength alloys to 0.250 in. for higher-strength alloys (to avoid overloading the stress-ageing equipment). The test-bars were mounted (vertically) in an "old-fashioned" vertical creep-testing furnace, with temperature control to within 1° C. The junctions of the control and check thermocouples were placed midway along the length of the reduced section of the tensile bar specimens. The creep furnace was resistance-heated and wound to compensate for end radiation, giving a constant temperature over a 12 in. zone with the test-bars in the centre. A combination of levers and pulleys gave a 1000 : 1 ratio for the stress applied to the reduced section of the bar relative to the load applied to the weight spindle outside the furnace. Each stress-ageing furnace accommodated four test-bars. The specified stresses were applied for the stated times at the chosen constant temperatures. Each line of tensile data reported in the subsequent stress-ageing tables is the average of test data from three treated bars. The reported electrical conductivities were measured on the reduced section of the treated tensile bars. All tensile tests of the stress-aged bars (and the untreated standards) were carried out by the staff of the Testing Division of the Schenectady Works Laboratory according to standard practice, yielding automatically recorded stress/strain curves. The tabulated tensile-property data are derived from the recorded stress/strain curves according to standard definitions (shown diagrammatically in Fig. 9).

Before considering in detail the results of stress-ageing, it will be helpful briefly to present the effects of this new treatment on some copper-, iron-, and aluminium-base alloys. Such data provide the background for understanding stress-ageing and justify the tentative claims made for the treatment. Much research remains to be done, however, before stress-ageing can be correctly understood.

III.—STRESS-AGEING OF COPPER-BASE ALLOYS.

Of the eight commercial copper alloys studied, seven were in the cold-worked condition. The only difference between cold-worked and annealed single-phase solid-solution alloys is that the former will withstand higher stresses and will therefore show greater response to stress-ageing. The alloys studied are listed in Table I, while Tables II-VI give the results obtained on the individual alloys with different stress-ageing treatments.

TABLE I.—*Copper-Base Alloys.*

Alloy Ref. No.	Grade and Composition	Condition
A1	70 : 30 Brass	Cold reduced 36%
A2	70 : 30 Brass	Cold reduced 52%
A3	85% Cu-13.25% Zn-1.75% Pb Alloy *	Cold reduced 35%
A4	85% Cu-13.25% Zn-1.75% Pb Alloy *	Cold reduced 50%
A5	5% Sn Phosphor Bronze	Cold reduced 60%
A6	10% Sn Phosphor Bronze	Cold reduced 60%
A7	99% Cu-1% Cd Alloy	Cold reduced 60%
A8	88.5% Cu-8.3% Al-2.9% Fe-0.3% Ni Alloy	Hot extruded

* Grade known as "Hardware Bronze".

TABLE II.—*Stress-Aged Properties of Commercial 70 : 30 Brass.*

Line Ref. No.	Stress-Ageing Treatment			Proportional Limit, lb./in. ²	0.2% Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elongation, %	Reduction of Area, %
	Stress, lb./in. ²	Time, hr.	Temperature, ° C.					
Cold Reduced 36%.								
A1	none	28,500	54,450	69,150	17	84
1	28,500	4	175	33,600	62,250	70,700	19.5	80
2	40,000	4	175	41,900	61,400	71,200	18	78
3	54,100	4	175	54,300	66,500	71,750	21	75
4	54,100	20	175	56,500	66,700	71,700	16	71
5	40,000	4	200	45,200	65,000	71,300	18	71
6	54,000	4	200	56,800	66,500	70,000	15	49
7	54,000	4	225	57,500	67,000	69,000	8	35
Cold Reduced 52%.								
A2	none	28,400	69,800	86,750	13	80
8	28,400	4	175	39,200	74,450	87,250	11.5	75
9	40,000	4	175	49,000	80,000	88,500	11.5	73
10	54,100	4	175	60,400	85,400	88,700	12	73
11	69,800	20	175	71,000	86,800	88,750	10	71
12	40,000	4	200	55,200	87,400	90,000	11	71
13	54,000	4	200	60,200	87,400	89,800	11	71
14	54,000	4	225	68,400	88,000	88,500	10	61

TABLE III.—*Stress-Aged Properties of Commercial Hardware Bronze*
(85% Cu-13.25% Zn-1.75% Pb).*

Line Ref. No.	Stress-Ageing Treatment			Proportional Limit, lb./in. ²	0.2% Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elonga- tion, %	Reduc- tion of Area, %
	Stress, lb./in. ²	Time, hr.	Tempera- ture, ° C.					
Cold Reduced 35%.								
A3	none	23,600	60,800	61,000	10	66
1	54,000	4	175	55,300	60,400	60,400	10	60
2	40,000	4	200	44,000	60,000	60,300	11	60
3	54,000	4	200	53,400	58,300	58,300	10	60
4	40,000	4	225	42,500	58,750	59,400	12	60
5	54,000	4	225	broke in furnace—3 hr.			7	48
6	40,000	4	250	44,100	57,800	58,350	12.5	60
7	40,000	4	275	42,850	53,700	55,650	10	48
Cold Reduced 50%.								
A4	none	27,350	75,000	76,200	8.5	66
8	54,000	4	175	60,000	75,000	75,700	9	60
9	40,000	4	200	51,900	74,800	75,500	9	60
10	63,500	4	200	60,900	74,000	75,000	10	60
11	40,000	4	225	49,600	72,350	74,500	10	60
12	63,500	4	225	63,100	71,900	72,750	9.5	48
13	40,000	4	250	48,400	71,500	72,600	9.0	60
14	40,000	4	275	50,300	69,300	71,250	10	55

* In the case of this alloy free lead permits ready flow for stresses above the elastic limit during the tensile test, thus masking what would otherwise probably be increased 0.2% offset yield strengths resulting from stress-ageing.

TABLE IV.—*Stress-Aged Properties of Commercial Phosphor Bronzes.*

Line Ref. No.	Stress-Ageing Treatment			Proportional Limit, lb./in. ²	0.2% Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elongation, %	Reduction of Area, %
	Stress, lb./in. ²	Time, hr.	Temperature, ° C.					
Cold Reduced 60% (95% Cu-5% Sn).								
A5	none	39,400	86,500	87,550	14	76
1	39,400	4	175	56,200	82,050	86,550	17.5	76
2	45,000	4	175	58,350	83,300	86,300	15	76
3	75,000	4	175	75,200	86,000	86,800	17	76
4	45,000	4	200	56,250	80,350	86,400	18.7	76
5	75,000	4	200	73,250	82,000	87,000	20	76
6	45,000	4	225	58,600	78,300	85,800	22	76
7	75,000	4	225	74,500	80,200	85,050	19.5	76
Cold Reduced 60% (90% Cu-10% Sn).								
A6	none	57,400	114,000	133,500	8.5	61
8	60,000	4	175	74,000	119,000	132,000	11	50
9	114,000	4	175	112,000	131,500	136,600	11	48
10	60,000	4	200	70,300	116,000	130,000	10	41
11	114,000	4	200	114,000	127,000	132,000	10	43
12	114,000	4	225	116,000	135,000	147,000	4	29

TABLE V.—*Stress-Aged Properties of Commercial Cadmium Copper*
(99% Cu-1% Cd).

Line Ref. No.	Stress-Ageing Treatment			Proportional Limit, lb./in. ²	0.2% Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elonga- tion, %	Reduction of Area, %
	Stress, lb./in. ²	Time, hr.	Tempera- ture, ° C.					
Cold Reduced 60%.								
A7	none	32,150	69,800	70,100	10	76
1	32,150	4	175	53,650	72,350	72,350	11	74
2	40,000	4	175	49,500	71,100	71,100	11	73
3	64,800	4	175	57,100	70,550	70,550	9.5	71
4	40,000	20	175	53,100	70,000	70,000	10	71
5	40,000	4	200	57,750	72,900	72,900	9.4	69
6	64,800	4	200	65,600	71,900	71,900	8.6	68
7	64,800	4	225	66,700	71,800	71,800	12.5	68

TABLE VI.—*Stress-Aged Properties of Commercial Aluminium Bronze*
(88.5% Cu-8.9% Al-2.9% Fe-0.30% Ni).

Line Ref. No.	Stress-Ageing Treatment			Proportional Limit, lb./in. ²	0.2% Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elonga- tion, %	Reduction of Area, %
	Stress, lb./in. ²	Time, hr.	Temperature, ° C.					
Hot Extruded.								
A8	none	25,000	32,950	81,100	40	60
1	25,000	4	175	26,600	32,100	80,500	42	62
2	32,000	4	175	34,700	36,200	80,000	35	60
3	32,000	4	200	32,250	34,200	80,200	39	61
4	32,000	20	200	34,600	36,200	81,000	35	54
5	32,000	4	225	31,400	33,250	80,000	41	62
6	32,000	4	250	33,000	35,100	81,100	37	58

1. *Effect on Electrical Conductivity.*

Table VII shows the effects on the electrical conductivity of two outstanding stress-ageing treatments for each alloy. In each case the percentage increase shown in the right-hand column is about double that which would be due to plain full annealing. This increase in electrical conductivity, coincident with increased strength properties *and* increased (or constant) elongation, would seem to indicate that a strained-lattice-induced precipitation might be taking place in these hitherto "un-heat-treatable" alloys.

2. *Effect on Physical Properties.*

The results of stress-ageing as applied to copper-base alloys are summarized in Table VIII, which shows that such treatments alter the

TABLE VII.—*Effect of Stress-Ageing Treatments on Electrical Conductivity of Copper Alloys.*

Line Ref. No.	Alloy and Condition	Elect. Conductivity,* %	Stress-Ageing Treatment			Elect. Conductivity, %	Increase, %
			Stress, lb./in. ²	Time, hr.	Temp., ° C.		
1X 1Z	70 : 30 Brass 36% Cold Work	} 21·6	40,000	4	200	27·5	27
			54,000	4	200	27·8	29
2X 2Z	70 : 30 Brass 52% Cold Work	} 21	54,000	4	175	27·1	30
			54,000	4	225	28·4	35
3X 3Z	Hardware Bronze 35% Cold Work	} 29·6	54,000	4	200	32·6	10
			40,000	4	275	34·8	19
4X 4Z	Hardware Bronze 50% Cold Work	} 29·2	63,500	4	200	35·3	21
			40,000	4	275	35·4	21
5X 5Z	5% Sn Phosphor Bronze 60% Cold Work	} 16·3	75,000	4	175	20·7	27
			45,000	4	225	21·7	33
6X 6Z	10% Sn Phosphor Bronze 60% Cold Work	} 8·2	114,000	4	175	10·4	27
			114,000	4	225	10·5	30
7X 7Z	99% Cu-1% Cd 60% Cold Work	} 69·4	40,000	4	200	83·0	20
			64,000	4	200	83·1	20
8X 8Z	Al Bronze No Cold Work	} 11·9	32,000	4	200	12·1	2
			32,000	20	200	12·1	2

* Expressed as a percentage of that of pure copper.

TABLE VIII.—*Effects of Stress-Ageing Treatments on Physical Properties of Copper Alloy Spring Materials.*

No.	Alloy	Condition	Proportional Limit, lb./in. ²	Elongation, %	Elect. Conductivity,† %
1	70 : 30 Brass	52% C.W.*	28,400	13	21
2	99% Cu-1% Cd	60% C.W.	32,150	10	70
3	5% Sn Phosphor Bronze	60% C.W.	39,400	14	16
4	10% Sn Phosphor Bronze	60% C.W.	57,400	8·5	8
5	Cu-2% Be	Heat-treated	65,000	1	21
6	99% Cu-1% Cd	Stress-aged	66,700	12·5	83
7	70 : 30 Brass	Stress-aged	71,000	10	27
8	5% Sn Phosphor Bronze	Stress-aged	75,200	17	21
9	10% Sn Phosphor Bronze	Stress-aged	114,000	10	10

* C.W. = Cold-worked, commercial alloy.

† Expressed as a percentage of that of pure copper.

engineering evaluation of commercial alloys. The elastic properties which are basic to engineering design, are well typified by the proportional limit. In the field of copper alloy spring materials an alloy of copper containing 2% beryllium and 0.5% cobalt or nickel is quite outstanding. Listing the proportional limit, percentage elongation, and percentage electrical conductivity, Table VIII compares some commercial copper alloys (with and without stress-ageing) with the copper-2% beryllium alloy. The commercial materials are cold-worked solid-solution alloys, whereas the copper-beryllium alloy is precipitation-hardened. The order of listing in Table VIII is that of increasing proportional limit (or useful strength). It is readily seen why the copper-beryllium alloy (No. 5) is superior to the ordinary commercial alloys (Nos. 1, 2, 3, 4). However, when they are stress-aged, the copper-cadmium alloy, 70 : 30 brass, and 5% tin bronze (Nos. 6, 7, 8) become highly competitive in spring properties with the commercial beryllium copper, while the 10% tin bronze is outstanding. An additional feature of considerable engineering and economic importance is that all the stress-aged alloys have a much higher ductility than beryllium copper; they can therefore be formed from stress-aged strip and wire, whereas beryllium copper must be formed in the solution-quenched condition and carefully precipitation-aged after forming.

3. Effect of Stress-Ageing on Types of Fracture in Tensile Testing.

In many cases, stress-ageing drastically alters the type and surface of the fractures obtained in subsequent tensile tests. Examples are as follows :

(a) 70 : 30 Brass, Cold Reduced 36% (Table II).

For this material, the reduction of area decreases progressively with increase in stress, increase in time at ageing temperature, and increase of ageing temperature. In fact, for stress-ageing at 225° C. (line 7, Table II), the marked decrease in elongation and reduction of area indicate embrittlement. The fractures show the following gradation :

In the usual commercial condition (line A1), the fracture has the normal, rather smooth, cup-and-cone appearance. After the treatments listed in lines 1-5, the normal cup-and-cone grades into a ragged fracture, in each case with a fine "honeycomb" roughened surface. After line 6 treatment, the fracture is a rough 45° shear. For line 7 the fracture is transverse and ragged; a brittle type of break that corresponds with the sharp decrease in elongation and reduction of area.

(b) 70 : 30 Brass, Cold Reduced 52% (Table II).

For this material the reduction of area decreases progressively with increases in stress-ageing severity, much as for the same alloy cold worked only 36%. The types of fracture parallel those reported for A1 (Table II), except that the changes are delayed somewhat for A2 in that the fracture corresponding to line 14 shows a 45° shear fracture, corresponding to the fracture for line 6 (A1). It might thus be expected that embrittlement would develop for A2 (52% cold work) were it to be stress-aged at 250° C.

(c) Copper-1% Cadmium Alloy (Table V).

The reduction of area decreases slightly while the type of fracture changes in a peculiar manner. Fractures, as related to the treatments detailed in Table V, are as follows :

Treatment	Type of Fracture
Line A7	Normal cup-and-cone.
Lines 1 and 2	Double cup-and-cone.
Lines 3-7	Perfect spirals.

4. Effect of Stress-Ageing on Microstructure.

Stress-ageing clearly affects the microstructure. It was also noted that it took longer to develop the structure of stress-aged material by etching : about 5 to 10 times as long for stress-aged 70 : 30 brass as for the plain cold-worked condition.

As a most marked example of stress-ageing, the 36% cold-worked brass, stress-aged under 54,000 lb./in.² for 4 hr. at 225° C. (line 7, Table II) was chosen. The etching reagent was potassium dichromate. Both bright-field illumination and polarized light were used at a magnification of 2000, and the photomicrographs are reproduced in Figs. 1 and 2 (Plates XXXI and XXXII). Whereas cold-worked brass showed little precise detail with bright-field illumination, polarized light proved far more revealing. From a comparison of Figs. 1 (a) and 2 (a), it is evident that the plain cold-worked material cannot be sharply focused, while the stress-aged structure lends itself to sharp focusing even at a high magnification. Comparing Figs. 1 (b) and 2 (b), it seems quite apparent that stress-ageing causes "spheroidization" or segmentation of the slip bands. The exact nature of this change in structure is not yet known, and, so far, investigations by both X-rays and the electron microscope have failed to yield any further information. It may be assumed, tentatively, that stress-ageing results in a mosaic of almost sub-microscopic strain-volume domains within which strain-induced solid-state reactions may develop.

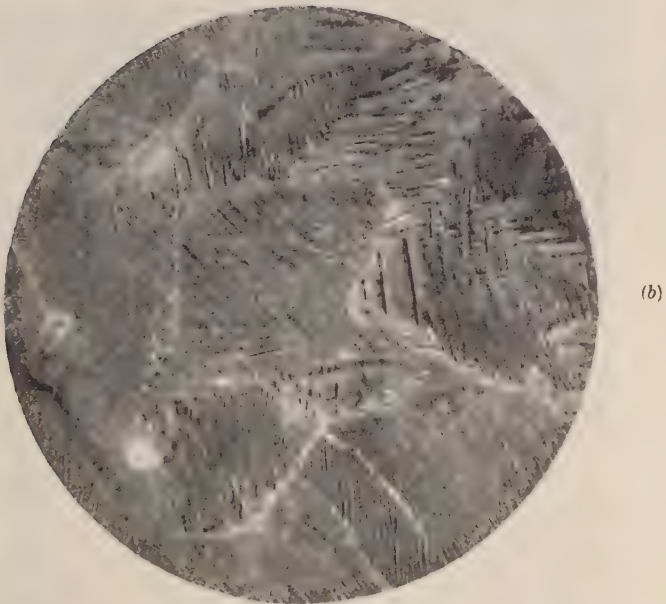
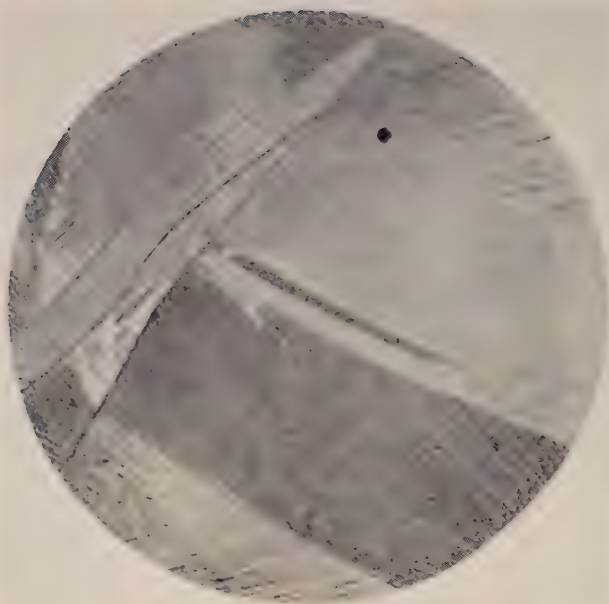
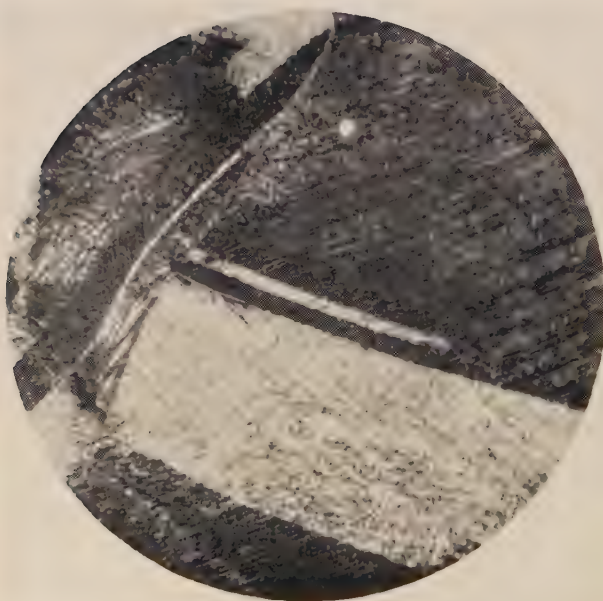


FIG. 1.—70 : 30 Brass, as Cold Reduced 36%. Photographed (a) with bright-field illumination; (b) using polarized light. $\times 2000$. Reduced one-half linear in reproduction.

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(a)



(b)

FIG. 2.—70 : 30 Brass, Stress-Aged under 54,000 lb./in.² for 4 hr. at 225° C. Photographed (a) with bright-field illumination; (b) using polarized light. $\times 2000$. Reduced one-half linear in reproduction.

5. An Explanation of the Stress-Ageing Effects in Single-Phase Brasses and Bronzes.

Stress-ageing appears to result in simultaneous increases in tensile properties, elongation, electrical conductivity, &c. These effects may be caused, in some stress-aged solid-solution phases, by (lattice distortion) "strain"-induced precipitation (or disorder-to-order changes, as the case may be) within localized minute strain-lattice (-volume) domains.*

A rationalized picture, based on the observed data, is presented in Fig. 3 for stress-aged (strain-induced) precipitation in the α -tin-bronzes.† The conventional temperature/composition diagram for copper-tin alloys is shown in the *TOC* plane. *PP'* is the pressure axis for the 3-variable system of pressure, temperature, and concentration inherent to the Phase Rule. For the solid state it is logically possible to use "+ pressure" for compressive strain (contracted lattice) and "- pressure" for strain in tension (expanded lattice). Although the strain gradients in stressed metal cannot yet be quantitatively measured, the applied stress (in the absence of any accompanying permanent deformation) can be plotted along the *P* axis, as from *O* to *D*.

Complete recrystallization, relief from strain, reversion from strain-ageing, and reversion from stress-ageing, all are brought about by heating at temperatures in excess of about 350° C., with the restoration of plain (undistorted) α phase for alloys containing less than 14% tin. However, the practical effect on engineering properties is induced by stress-ageing at temperatures in the range 175°-250° C. (Table IV). The benefit is largely eliminated by heating at temperatures above 300° C. Therefore, the effective *PTC* volume is indicated by the space within *OABD* and *O'A'B'D'* (Fig. 3).

Just as a concave *solvus line* indicates precipitation from a solid-solution field in the conventional temperature/composition "equilibrium" diagram, the *solvus surface* (shaded in Fig. 3) *yB'AA'* indicates stress-ageing-induced precipitation. The solvus surface is generated through the curves *mm*, *nn*, *rr*, *ss*, *xx*, and *yy* to indicate the effects of increased solute (tin) content and increased strain (from the

* When a directional load is applied (either tension or compression), three-dimensional gradients of lattice expansion and lattice contraction are set up as a result of such factors as: (1) difference between direction of individual grain orientation and direction of applied load, (2) shape and dimensions of piece being treated, (3) type of crystal lattice of the solid-solution phase, (4) lattice "imperfections", such as inclusions, lattice vacancies, slip bands, minor deviations of orientation (such as lattice mosaics), &c. These three-dimensional lattice distortion gradients have, for the present purpose, been termed "strain-volume domains" or "strain-lattice domains".

† The same explanation, in more detail, as applied to the changes effected by plain ageing of cold-worked brasses and bronzes, is given elsewhere.¹

applied stress of stress-ageing) on the quantity of stress-ageing-induced precipitation and on the temperature for re-solution (annealing). The intersection of the solvus surface with the pressure/composition plane (*POC*) is shown in the inset to Fig. 3.

The concept of stress-ageing- (or strain-) induced precipitation is

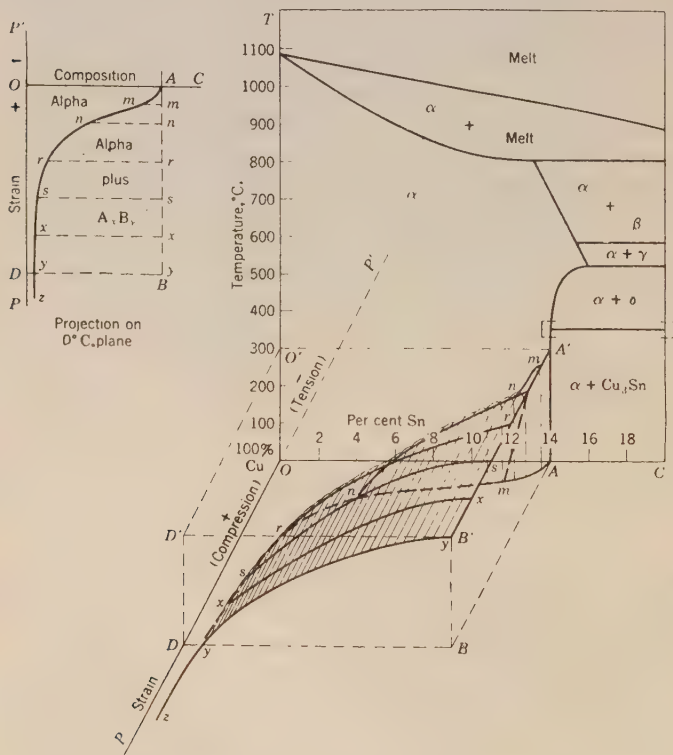


FIG. 3.—Stress-Ageing and the Phase Rule for Copper-Tin Alloys.

comparable with the concept of plain temperature/composition (*TOC*) precipitation. Just as a solution quench for some systems will retain a metastable supersaturated solid solution at room temperature, and artificial ageing, at some elevated temperature, is necessary to permit the required atomic diffusion for precipitation, *strain* (induced by stress-ageing) may exert a similar effect. Thus, if a possible precipitation (or alternatively disorder-to-order) reaction will result in lattice contraction, a localized strain-gradient volume (individual

"pressure" system) under compressive strain would favour such a reaction, whereas localized strain in tension would oppose it. The reverse effects of strain apply to a reaction that results in lattice expansion. For many systems, rates of diffusion at room temperature would be too slow for any practical effect, whereas elevated temperature (below that resulting in recrystallization) and time at such temperature could effect strain- (lattice-distortion-) induced precipitation. Thus, in Fig. 3, the shaded solvus surface delineates the surface of temperature below which stress-ageing-induced precipitation may take place and above which re-solution takes place, previous to (or coincident with) structural recrystallization (or annealing). Thus time at stress-ageing temperature may be a most important factor.

(It should be noted that, for visual presentation, the solvus surface has been located in the *TPC* quadrant of Fig. 3, whereas, if the reaction is induced by an expanded or extended lattice, the solvus surface would occur in the *TP'C* quadrant, behind the conventional *TOC* plane.)

IV.—STRESS-AGEING OF IRON-BASE ALLOYS.

The five iron-base alloys studied are as follows :

- (1) 18 : 8 Stainless Steel, cold-worked 38%.
- (2) 64% Fe-36% Ni, annealed.
- (3) 79% Fe-19% Ni-2% Cr, annealed.
- (4) 71% Fe-18% Ni-11% Cr, annealed.
- (5) Ni-Span C. (42% Ni-5.5% Cr-2.5% Ti-0.06% C-0.40% Mn-0.50% Si-0.40% Al, balance iron).

The stress-ageing properties of 18 : 8 stainless steel are shown in Table IX. Lines 2, 3, and 4 give the results of cold working during creep under high stresses at room temperature. For stainless steel, stresses above the proportional limit (for 4 hr. at 25° C.) do result in some strengthening, due simply to cold working as the elongations are decreased. The proportional-limit stress has no effect (as was to be expected). However, it must be remembered that the cold-work strengthening effect from plastic deformation of creep would be much less at elevated temperatures than at room temperature. Thus, for this stainless steel, the results of treatment from 400° to 600° C. under stress are largely due to stress-ageing. Since the steel is not stabilized, it is subject to some strengthening through precipitation of carbides. This effect is measured by plain ageing (in the absence of any applied stress), with the results given in Table X. Overall analysis of the stainless

TABLE IX.—*Properties of Stress-Aged 18% Cr-9% Ni Stainless Steel, Cold Worked 38%.*

Line Ref. No.	Stress-Ageing Treatment			Proportional Limit, lb./in. ²	0.2% Offset Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elongation, %.	Reduction of Area, %
	Stress, lb./in. ²	Time, hr.	Temp., ° C.					
1	none	72,300	178,500	193,200	7.5	37
2	72,300	4	25	72,200	178,600	193,800	7.5	37
3	90,000	4	25	105,000	174,600	194,200	7.0	36
4	150,000	4	25	120,000	176,600	192,900	2.0	30
5	90,000	$\frac{1}{4}$	400	133,400	188,900	202,200	8.5	36
6	90,000	$\frac{1}{2}$	400	138,700	187,700	202,600	8.5	38
7	90,000	$\frac{3}{4}$	400	139,700	188,200	201,900	8.5	38
8	90,000	1	400	138,300	188,600	202,600	8.5	38
9	90,000	2	400	140,000	188,100	203,100	8.5	38
10	90,000	4	400	142,000	191,000	205,400	8.5	39
11	90,000	4	450	136,000	197,600	204,000	8.5	42
12	90,000	4	500	134,000	193,000	197,300	8.5	40
13	90,000	4	550	128,000	170,000	182,000	6.0	46
14	90,000	4	600	114,000	159,000	176,500	13.5	42
15	150,000	4	400	154,000	206,000	208,800	8.5	42
16	150,000	4	450	Bar broke in furnace.				
17	150,000	4	500	Bar broke in furnace.				

TABLE X.—*Properties of Plain-Aged 18% Cr-9% Ni Stainless Steel, Cold Worked 38%.*

Line Ref. No.	Plain Ageing Treatment (No applied stress)		Proportional Limit, lb./in. ²	0.2% Offset Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elongation, %	Reduction of Area, %
	Time, hr.	Temp., ° C.					
1	Un-aged		72,300	178,500	193,200	7.5	37
2	4	400	96,500	180,000	197,000	7.5	63
3	4	450	93,000	181,000	195,000	7.5	60
4	4	500	92,800	170,000	183,000	6.0	61
5	4	550	88,000	171,000	184,000	7.5	62

steel data shows that the strengthening due to stress-ageing treatments is attributable chiefly to the stress-ageing reaction, as is indicated also by the higher elongations developed by stress-ageing.

The three single-phase annealed solid-solution alloys of iron are free from complications and are especially interesting (see Table XI), since they prove that cold work previous to stress-ageing possesses no inherent value as a prerequisite for the stress-ageing reaction. The most pronounced stress-ageing effect so far noted is for Alloy No. (4)

(lines 13-18 in Table XI) wherein stress-ageing yields a proportional limit higher (line 16) than its initial tensile strength (line 13).

Ni-Span C is a precipitation-hardening (constant modulus) alloy among whose unusual properties is the fact that its inherent precipitation reaction is sharply effective upon ageing *above* 500° C. Thus, the effects noted (in lines 2 and 3, Table XII) for stress-ageing at 400° and 500° C. appear to be due to stress-ageing alone. The stress-ageing effects for the fully heat-treated Ni-Span C (lines 5, 6, 7) seem to be caused by further precipitation, strain-induced by stress-ageing of the solid-solution matrix of the aged material.

Some research has been conducted on stress-ageing of precipitation-hardening alloys in the solution-quenched condition and in the temperature range for inherent precipitation. This phase of the study of stress-ageing is incomplete and will be described at a later date.

TABLE XI.—*Stress-Aged Properties of Three Annealed Iron-Base Solid-Solution Alloys.*

Line Ref. No.	Stress-Ageing Treatment			Creep *	Proportional Limit, lb./in. ²	0.2% Offset Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elonga- tion, %	Reduction of Area, %
	Stress, lb./in. ²	Time, hr.	Temp., ° C.						
64% Fe-36% Ni.									
1	none	25,000	40,000	70,000	35	65
2	25,000	4	400	0	45,800	68,000	84,500	21	81
3	40,000	4	400	0	56,500	69,500	84,500	21	81
4	40,000	20	400	0.001	57,200	65,400	81,200	20	80
5	25,000	4	500	0.005	47,800	59,800	80,700	25	78
6	40,000	4	500	0.300	52,600	68,800	84,800	16	77
79% Fe-19% Ni-2% Cr.									
7	none	30,000	45,000	85,000	40	60
8	30,000	4	400	0	68,500	84,000	122,000	32	71
9	45,000	4	400	0	75,400	85,600	121,800	29	67
10	45,000	20	400	0	69,200	80,000	116,000	40	73
11	30,000	4	500	0	62,200	82,500	120,000	30	69
12	40,000	4	500	0	65,800	75,700	117,500	38	69
71% Fe-18% Ni-11% Cr.									
13	none	25,000	40,000	85,000	42	55
14	25,000	4	400	0	59,000	86,750	110,000	25	65
15	40,000	4	400	0	74,300	101,500	120,000	36	66
16	65,000	20	400	0	89,200	101,500	117,000	20	60
17	25,000	4	500	0	42,700	48,300	99,800	22	63
18	40,000	4	500	0	72,800	99,500	120,000	21	62

* Creep, during stress-ageing, reported as in./in. length.

TABLE XII.—*Stress-Aged Properties of Ni-Span C, Precipitation-Hardening Alloy.*

Line Ref. No.	Stress-Ageing Treatment			Creep *	Proportional Limit, lb./in. ²	0.2% Offset Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elonga- tion, %	Reduc- tion of Area, %
	Stress, lb./in. ²	Time, hr.	Temp., ° C.						
Plain Solution-Treated.									
1	none	15,000	35,000	90,000	40	60
2	35,000	4	400	0	50,000	51,000	93,000	38	66
3	35,000	4	500	0	52,200	54,200	99,800	39	66
Precipitation-Aged.									
4	none	65,000	115,000	165,000	16	30
5	90,000	4	400	0	99,000	123,000	164,000	17	45
6	115,000	4	400	0.08	131,500	135,000	164,000	15	50
7	65,000	4	500	0	94,200	123,000	164,000	16	40

* Creep, during stress-ageing, reported as in./in. length.

V.—THE EFFECT OF STRESS-AGEING ON WROUGHT ALUMINIUM ALLOYS.

In a similar manner and with equal detail (as for the copper-base and iron-base alloys), the effects of stress-ageing on the properties of eleven wrought aluminium alloys have been studied. Table XIII gives the chemical composition of these alloys. Details of heat-treatment are given in Table XIV. It will be noted that three of the alloys were cold worked to improve their tensile properties, while eight were used in the age-hardened condition.

TABLE XIII.—*Chemical Compositions of Wrought Aluminium Alloys.*

Alloy	Cu, %	Si, %	Mn, %	Mg, %	Zn, %	Ni, %	Cr, %	Pb, %	Bi, %
2S	Up to 1% total impurities								
3S	1.2
11S	5.5	0.5	0.5
14S	4.4	0.8	0.8	0.4
17S	4.0	...	0.5	0.5
18S	4.0	0.6
24S	4.5	...	0.6	1.5
25S	4.5	0.8	0.8
52S	2.5	0.25
61S	0.25	0.6	...	1.0	0.25
75S	1.6	2.5	5.6	...	0.3

TABLE XIV.—*Heat-Treatments Applied to Wrought Aluminium Alloys Before Stress-Ageing.*

Alloy.	Solution Temp., ° C.	Precipitation Ageing	
		Temp., ° C.	Time, hr.
11S-T8	520	165	12
14S-T6	505	170	8-12
17S-T	505	R.T.	...
18S-T61	505	170	8-12
24S-T36	495	190	8-10
25S-T6	515	170	8-12
61S-T6	520	160-175	6-20
75S-T6	465	120	22-26

1. Representative Stress-Ageing Data.

Representative stress-ageing data for several of the individual alloys are shown in Figs. 4-8.

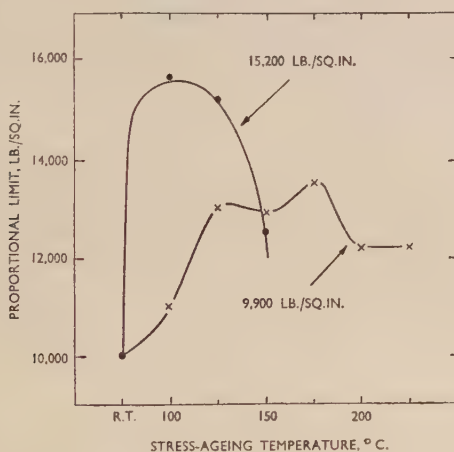


FIG. 4.—Effect of Stress-Ageing on the Proportional Limit of Alloy 3S- $\frac{1}{2}$ H.

2. Evaluation of Stress-Ageing Data.

The stress-ageing data for all the aluminium alloys are contained in Table XV. In each case, the first line of data gives the properties of the alloy in its "as-received" condition of standard treatment (either cold worked or heat-treated as the case may be); the second line gives the properties after stress-ageing at a chosen temperature (and stress); the third line gives the properties after ageing (or re-ageing, as the case

may be) the alloy at the same temperature without the applied stress; and the fourth line gives the properties after prolonged plain ageing.

The chief purpose of Table XV is to set out representative data for

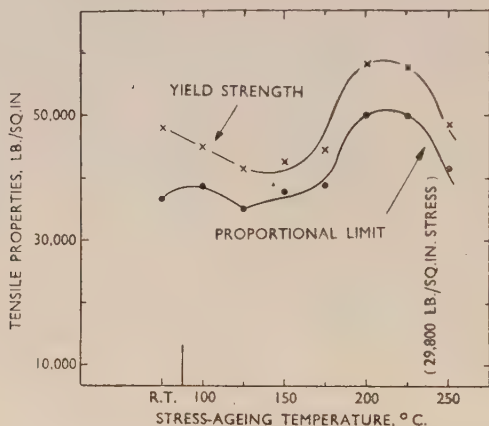


FIG. 5.—Effect of Proportional Limit (36,500 lb./in.²) Stress-Ageing on Alloy 17S-T.

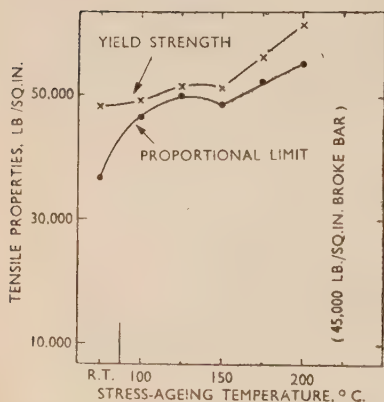


FIG. 6.—Effect of Yield Strength (48,000 lb./in.²) Stress-Ageing on Alloy 17S-T.

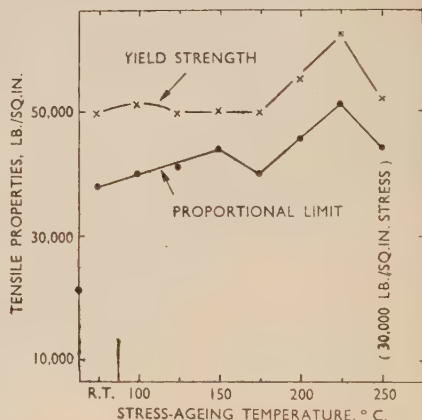


FIG. 7.—Effect of Proportional Limit (38,000 lb./in.²) Stress-Ageing on Alloy 24S-T.

each alloy and to prove the real effects and true existence of stress-ageing. The data cited are not necessarily the maximum results of stress-ageing in all cases. It is obvious from Table XV that, in general, the effect of stress-ageing for heat-treated alloys is opposite to that of plain ageing

(in the absence of applied stress) at the same temperature. Marked variation in shape of the stress/strain curves is also indicated. In a few instances "double-ageing" * does effect some increase in properties,

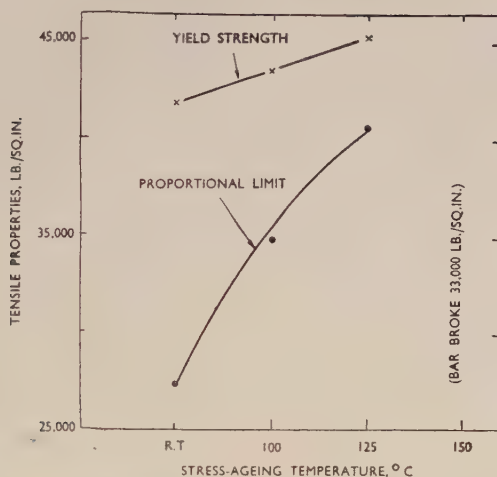


FIG. 8.—Effect of Yield Strength (41,000 lb./in.²) Stress-Ageing on Alloy 25S-T.

probably for the same reason but never to the same extent as stress-ageing.

3. *Maximum Results for Individual Alloys.*

From the present studies of stress-ageing, it has been noted that the improvement in physical properties is greater with higher applied stress, with higher solute-metal contents, with longer times at temperature, and with higher temperatures (until such a high temperature is reached that the annealing tendency exceeds the stress-ageing reaction). Thus aluminium alloys, with their lower inherent elastic properties, lower solute-metal contents, and lower recrystallization temperatures, cannot be expected to yield nearly such great increases in physical properties as were observed for the stress-aged copper-base and iron-base alloys. However, improvements of real engineering value are realized for some of the aluminium alloys, while all respond in some degree to stress-ageing treatment.

Alloy 11S-T8, for example, is a heat-treatable alloy to which 0.5% lead and 0.5% bismuth have been added for free machinability. Other effects of lead and bismuth are to increase the notch sensitivity, decrease

* For definition see ref. 2.

TABLE XV.—*Evaluation of Stress-Ageing Data for Aluminium Alloys.*

Alloy	Treatment *	Proportional Limit, lb./in. ²	0.2% Offset Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elongation, %
2S-½H	As cold worked	11,000	17,800	20,000	20
	Stress-aged, 11,000 lb./in. ² , 4 hr., 125° C.	13,600	17,700	19,500	21
	Plain aged, 4 hr., 125° C.	9,000	17,000	19,000	21
	Prolonged ageing, 125° C.	...	12,000	14,500	22
3S-½H	As cold worked	10,500	21,000	22,700	17
	Stress-aged, 15,200 lb./in. ² , 4 hr., 125° C.	15,200	21,000	21,700	18
	Plain aged, 4 hr., 125° C.	12,000	21,000	22,400	18
	Prolonged ageing, 125° C.	...	16,000	19,000	17
11S-T8	As heat-treated	32,500	44,600	55,700	12
	Stress-aged, 32,800 lb./in. ² , 4 hr., 125° C.	39,000	46,000	55,800	13
	Plain aged, 4 hr., 125° C.	29,000	43,000	55,500	12
	Prolonged ageing, 125° C.	...	20,000	30,000	25
14S-T	As heat-treated	43,800	55,300	65,700	13
	Stress-aged, 45,000 lb./in. ² , 4 hr., 175° C.	47,500	57,400	66,200	12
	Plain aged, 4 hr., 175° C.	43,300	53,900	62,200	10
	Prolonged ageing, 175° C.	...	22,000	27,000	30
17S-T	As heat-treated	36,500	48,000	66,000	24
	Stress-aged, 45,000 lb./in. ² , 4 hr., 200° C.	54,800	61,200	65,200	12
	Plain aged, 4 hr., 200° C.	38,600	56,700	64,000	12
	Prolonged ageing, 200° C.	...	11,000	17,000	33
18S-T	As heat-treated	36,050	47,500	59,100	13
	Stress-aged, 47,000 lb./in. ² , 4 hr., 125° C.	45,700	52,800	62,200	12
	Plain aged, 4 hr., 125° C.	32,000	47,900	58,700	12
	Prolonged ageing, 125° C.	...	45,000	50,000	12
24S-T	As heat-treated	38,000	49,750	69,300	18
	Stress-aged, 49,000 lb./in. ² , 4 hr., 175° C.	51,500	53,300	69,300	19
	Plain aged, 4 hr., 175° C.	38,700	51,000	69,000	18
	Prolonged ageing, 175° C.	...	25,000	30,000	24
25S-T	As heat-treated	27,300	41,800	59,100	24
	Stress-aged, 27,300 lb./in. ² , 4 hr., 200° C.	31,000	45,500	59,000	19
	Plain aged, 4 hr., 200° C.	28,500	41,800	56,000	13
	Prolonged ageing, 200° C.	...	13,500	19,000	35
52S-½H	As cold worked	17,500	26,000	32,800	16
	Stress-aged, 17,500 lb./in. ² , 4 hr., 175° C.	19,400	22,900	32,000	22
	Plain aged, 4 hr., 175° C.	15,600	22,200	32,000	21
	Prolonged ageing, 175° C.	...	12,000	20,000	60
61S-T	As heat-treated	34,800	41,000	47,500	12
	Stress-aged, 34,900 lb./in. ² , 4 hr., 150° C.	37,300	41,100	46,200	14
	Plain aged, 4 hr., 150° C.	30,000	40,300	47,200	16
	Prolonged ageing, 150° C.	...	29,000	31,000	18
75S-T	As heat-treated	57,700	71,500	82,000	11
	Stress-aged, 57,700 lb./in. ² , 4 hr., 150° C.	65,800	73,700	81,000	11
	Plain aged, 4 hr., 150° C.	56,000	70,000	79,600	11
	Prolonged ageing, 150° C.	...	22,000	28,000	32

* Prolonged ageing properties are typical tensile properties at elevated temperatures after prolonged heating at testing temperatures.

ductility somewhat, to cause rather erratic behaviour in the plastic range of stress, and to lower the thermal stability. For screw-machine stock these disadvantages are outweighed (on a cost basis) by the improved machinability. The notch sensitivity was indicated by the number of test-bars that broke in the gauge mark during tensile tests.

Although the presence of lead and bismuth structurally oppose stress-ageing (as in the case of leaded brass), stress-ageing is still effective for this alloy, increasing the proportional limit by 20%.

In Table XVI are recorded for each alloy the standard tensile

TABLE XVI.—*Maximum Stress-Ageing Effects for Aluminium Alloys.*

Alloy	Condition	Proportional Limit, lb./in. ²	Proportional Limit Change, %	0.2% Offset Yield Strength, lb./in. ²	Yield-Strength Change, %	Elongation, %	Elongation, Change, %
2S-½H	C.W.	11,000		17,850		20	
	S.A.	13,600	+25	17,700	0	21	+ 5
3S-½H	C.W.	10,000		21,000		17	
	S.A.	15,700	+57	21,100	0	18	+ 6
11S-T	H.T.	32,500		44,600		12	
	S.A.	39,000	+22	46,000	+ 3	13	+ 8
14S-T	H.T.	43,800		55,300		13	
	S.A.	51,000	+18	57,400	+ 4	15	+15
17S-T	H.T.	36,500		48,000		24	
	S.A.	51,800	+41	55,800	+16	22	— 8
18S-T	H.T.	36,050		47,500		13	
	S.A.	45,800	+25	51,300	+ 8	14	+ 8
24S-T	H.T.	38,000		49,750		18	
	S.A.	51,500	+35	53,300	+ 8	19	+ 5
25S-T	H.T.	27,300		41,800		24	
	S.A.	40,400	+48	45,000	+10	22	— 8
52S-¼H	C.W.	17,500		26,000		16	
	S.A.	25,200	+47	26,800	+ 4	19	+19
61S-T	H.T.	34,800		41,000		12	
	S.A.	38,900	+12	42,400	+ 4	13	+ 8
75S-T	H.T.	57,700		71,500		11	
	S.A.	65,800	+14	73,700	+ 3	11	0

C.W. = Cold Worked. H.T. = Heat-Treated. S.A. = Stress-Aged.

properties (first line) previous to stress-ageing and (second line) the respective *maximum* stress-aged properties. The relative changes (in %) are also noted for the proportional limit, the 0.2% offset yield strength, and the elongation.

The elastic properties of all the aluminium alloys are improved by stress-ageing (although less so than for the copper- and iron-base alloys). The increases in elastic properties are accompanied, with but three minor

exceptions, by increases in elongation. The initially high-strength alloys that show the greatest increases from stress-ageing contain about 4% copper and/or 1-2% magnesium.

4. Thermal Stability Under Stress.

It is now obvious that the thermal stability (maximum service temperature) of an alloy under stress may be very different from its thermal stability in the absence of stress. Thermal stability is here defined as the ability of an alloy to regain its initial room-temperature properties after exposure to elevated temperatures (with and without applied stress). The maximum temperature attained with the alloy subject to its initial proportional-limit stress, without subsequent loss of properties, is the criterion for the rating of the alloys in Table XVII.

TABLE XVII.—*Thermal Stability Under Stress.*

Alloy	Thermal-Stability Rating (S.A.)	Thermal Stability, under Stress, max. temp., °C.	Thermal Stability in Absence of Stress,* max. temp., °C.
25S-T	1	200	125
52S- $\frac{1}{4}$ H	2	200	140
24S-T	3	175	125
17S-T	4	175	125
14S-T	5	175	125
18S-T	6	175	125
3S- $\frac{1}{2}$ H	7	175	100
61S-T	8	150	120
11S-T8	9	150	100
75S-T	10	150	100
2S- $\frac{1}{2}$ H	11	125	100

* Thermal stability in the absence of stress derived from tables pp. 98-99, Alcoa 1947 Handbook. S.A. = Stress-aged.

On this basis, 25S-T is the best (200° C.), with the cold-worked alloy, 52S- $\frac{1}{4}$ H, surprisingly second, though it is a much lower-strength alloy. If marked reduction in elongation, indicating hot shortness and embrittlement, is not harmful to a specific application, then 17S-T and 24S-T may be rated at 225° C. The superiority of 25S-T also focuses attention on the alloy Al-Cu-Be³.

VI.—CONCLUSIONS ON STRESS-AGEING.

1. *Factual Bases.*

(1) All teaching and experience in the past indicated that the only way to strengthen solid-solution alloys was by cold working; moreover, that such cold-worked materials could not be further strengthened without greater cold reduction, such additional cold reduction being

progressively less effective. It has been shown above, however, for eight single-phase solid-solution copper-base alloys, four iron-base alloys, and three aluminium-base alloys, that these conclusions were in error.

(2) All teaching in the past has been to the effect that fundamental principles precluded the conception that heat-treating (ageing) under stress (as in tension) could establish any effective improvement in useful properties. It has been shown in the present paper that heat-treating under stress does have a marked effect, producing a really great improvement in subsequent engineering properties.

(3) In the case of any solid-solution structurally-dominated alloy, the facts reported here show that the most effective stresses are those in the range from the proportional limit to the 0.2% offset yield strength determined for the material in the condition before "stress-ageing". In certain cases, wherein the simultaneous creep (flow) is not appreciable, still higher stresses would be beneficial. Stresses of lower value than the proportional limit of the alloy are less effective and in most cases would not economically justify the special treatment.

(4) The beneficial effect of stress-ageing increases with increase in applied stress, increase in ageing temperature (until such a temperature is reached that the tendency to anneal exceeds the stress-ageing reaction), and increase in time at temperature of stress-ageing. In general, a period of 20 hr. accomplishes practically complete stress-ageing, although alloys with exceptionally slow diffusion rates would respond to longer ageing. An ageing period of 4 hr. normally produces about 90–95% of the "complete" effect, and would be very practical. In many cases, as short a time as $\frac{1}{2}$ hr. of stress-ageing may well lead to very useful and more economical results. The general range of most effective stress-ageing temperatures extends from somewhat below to somewhat above the temperature for softening with standard annealing; in other words, for 100° or more on either side of the recrystallization temperature.

(5) The beneficial effects of stress-ageing increase with increase in solute-metal content. However, relatively small amounts of alloy content (whether intentional additions or normal impurities) may be very effective, as in the data reported for the copper-1% cadmium alloy. The solid-solution and the precipitation-hardening wrought aluminium alloys are further examples of alloys of rather low solute-metal content. Similarly, the ferrite matrix of plain carbon steels contains varying small amounts of carbon, manganese, silicon, &c., and has a capacity for "stress-ageing".

(6) Since stress-ageing shows such marked value in solid-solution single-phase alloys, it is obvious that this new treatment will be effective

for alloys in which one or more solid-solution phases dominate the microstructure, as in the case of precipitation-hardening alloys. This is demonstrated for aluminium alloys 11S-T, 14S-T, 17S-T, 18S-T, 24S-T, 25S-T, 61S-T, and 75S-T. After precipitation-hardening of the aluminium alloys, relatively small amounts of solute metals remain in solution to provide stress-ageing effects, and the improvement of these alloys by stress-ageing ranges from 20 to 50%. Why, then, should 1% of cadmium in copper yield so much greater an improvement (100%)? The answer depends on the fact that cadmium is a "pseudo metal",

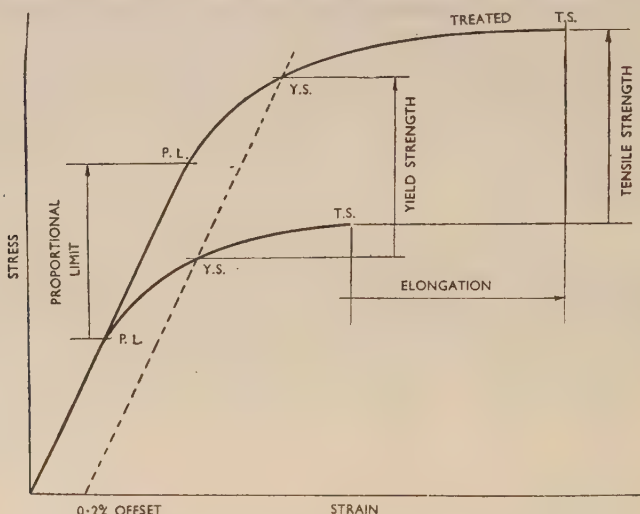


FIG. 9.—Effect of Stress-Ageing on Tensile Properties.

whereas most of the solute metals in the aluminium alloys are "transition metals".⁴

(7) *Maximum* stress-ageing for any specific alloy may effect the following increases in engineering properties: from 20 to 150% for the proportional (or elastic) limit, up to 100% for the 0.2% offset yield strength, up to 50% for the tensile strength, up to 75% for elongation, and up to 50% for electrical (and heat) conductivity.

(8) The effect of stress-ageing on tensile properties is shown in Fig. 9.

2. Theoretical Observations.

(1) Qualitatively, rates of diffusion in metals and alloys at room temperature increase relative to the specific melting points (or melting range), and thermal agitation of atoms within the crystal structure increases with temperature. Metals and alloys with higher melting

points and ranges have higher recrystallization temperatures and are more stable at room temperature when in the cold-worked condition. Thus cold-worked alloys of aluminium, copper, nickel, iron, &c., maintain their cold-worked structures at room temperature and up to higher temperatures until they definitely soften and recrystallize, whereas alloys of lead and most of the alloys of zinc recrystallize at or below room temperature. Thus alloys that recrystallize at or below room temperature cannot be stress-aged to any practical degree.

(2) Stronger lattice binding within the crystal structure results in higher melting temperatures, since greater thermal agitation at higher temperatures is required to break the interatomic linkage. Thus alloys with higher melting points will require greater applied stresses for maximum stress-ageing results. Therefore stresses for effects of practical value may exceed 20,000 lb./in.² for aluminium alloys, 40,000 lb./in.² for copper alloys, and 50,000–60,000 lb./in.² for alloys of iron, nickel, and cobalt.

(3) From theoretical observations (1) and (2), it follows that the stress-aged condition for any specific alloy will have about the same elevated-temperature stability as does its cold-worked condition. Thus, for complete relaxation or recovery from its stress-aged condition, the specific alloy will have to be reheated to about the temperature of its stress-ageing treatment in the absence of any externally applied load. (This has not been *proved* as yet. For alloys having recrystallization temperatures above room temperature, the stress-aged condition appears to be perfectly “stable” at room temperature.)

(4) A considerable change in crystal structure seems necessarily involved, but it probably takes place within submicroscopic strain-gradient volumes. It has been observed that stress-aged cold-worked structures take five to ten times as long to etch and give very sharp structures for clear focusing, whereas plain cold-worked structures cannot be sharply focused at magnifications as high as 2000. Variations in structure, such as segmentation of slip bands and apparent localized precipitation, have been observed but not identified. The structures are so fine and complicated that no satisfactory results have been obtained, so far, from investigation with X-rays and the electron microscope. At the present time the available data, together with the concept of pressure in the phase rule (tension being simply “negative pressure” for the elastic crystal structure), suggest the following possible (even probable) explanations of the stress-ageing reaction :

(a) Lattice-strain- (or distortion-) induced precipitation for the cold-worked (or annealed) copper-base alloys and for aluminium alloys 2S, 3S, and 52S.

(b) A further lattice-strain-induced precipitation for the previously precipitation-hardened aluminium alloys 11S-T, 14S-T, 17S-T, 18S-T, 24S-T, 25S-T, 61S-T, and 75S-T, and for Ni-Span C.

(c) A combination of lattice-strain-induced precipitation and allotropic transformation for cold-worked (and annealed) stainless steel.

(d) A lattice-strain- (maintained in all these cases by an externally applied stress) induced allotropic transformation ("martensite") for certain of the single-phase solid-solution iron-base alloys in the initially annealed (or cold-worked) condition.

(e) In some cases, a further possibility may be a strain-induced ordering reaction.

(f) The physical-property changes effected by stress-ageing appear to be far too great to be explained by stress-temperature-induced anisotropy of lattice-site vacancies.

3. Practical Methods of Stress-Ageing in Tension.

Several practical methods for stress-ageing appear to be immediately available :

(1) Formed springs of strip or wire may be compressed, extended, or deflected to the desired degrees of stress and the stressed spring may be raised to the required temperature for an effective time by high-frequency heating.

(2) Lengths of strip or wire may be stressed in tension and correctly heated by resistance methods (passing current through the stressed material), or in a muffle furnace.

(3) Probably the most economical (and the easiest) method appears to be that of "strand" stress-ageing. Commercial strand annealing is an established method of high efficiency and economy for the continuous annealing (softening) of strip and wire that have been cold worked. The strip or wire is drawn from loose-lying coils or free-running reels or spools, pulled through the annealing (softening) furnace, and re-coiled or re-wound at the furnace exit. Since the purpose of strand annealing is to produce practically "dead soft" strip and wire for subsequent forming or further cold reduction, the strand-annealed product must have very low strength properties. From the viewpoint of handling such soft material, the stress involved in pulling the free-running strip or wire through the furnace is kept as low as possible, far too low for any stress-ageing effects, especially in view of the fact that the practical annealing temperatures are considerably in excess of the recrystallization temperature and, therefore, by annealing practice,

too high for stress-ageing. If the conventional strand-annealing equipment be altered (by any one of a number of ways) to maintain the desired "high" stress and proper (lower) stress-ageing temperatures, the very desirable stress-aged properties can be developed for the chosen material, in whatever desired condition: annealed, cold worked, or heat-treated.

(4) Plate and rod stock of smaller sizes may be stress-aged as in (2) above, the chief limitation being the available means (capacity) for applying stress.

(5) Within the limitations of shape, size, least transverse-section area, and available capacity for stressing, various structural parts may be suitably stressed and aged under stress by high-frequency heating.

4. Practical Significance of Stress-Ageing.

(1) Conservation of material:

(a) Present operational stresses may be borne by half (or less) of the present cross-sections, if the operating parts are stress-aged.

(b) Present operating parts may support twice the present operational stress (or more), if the parts are stress-aged.

This 2:1 ratio applies for the many alloys that have the capacity to stress-age to at least double their original proportional and elastic limits. Lower savings apply to those alloys of smaller inherent stress-ageability.

(2) Stress-ageing treatments may alter the engineering evaluation of today's commercial alloys. This is exemplified in Table VIII (p. 208), wherein it is shown that stress-ageing permits such alloys as copper-1% cadmium and 70:30 brass to develop spring properties about equivalent to those of heat-treated beryllium copper.

(3) Such measured improvements in elastic properties, combined with the same (or higher) elongation, give promise that stress-ageing should also yield improved endurance properties and creep strength. It is suggested that the stress-ageing reaction may dominate the second stage of creep.

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The copper-base alloys used in the experiments were furnished by the American Brass Company, the stainless steel by the Allegheny-Ludlum Steel Corporation, the other four iron-base alloys by the H. A. Wilson Company, and the aluminium alloys by the Aluminum Company of America.

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THE INFLUENCE OF ALLOY CONSTITUTION 1278 ON THE MODE OF SOLIDIFICATION OF SAND CASTINGS.*

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

Continuing previous work (*J. Inst. Metals*, 1950, **77**, 1), the paper describes an experimental study of the mechanism of solidification of castings in a number of metals and alloys differing widely in respect of constitution, freezing temperature, freezing range, and thermal properties. The solidification of cylinder and slab castings in each material was investigated by making temperature measurements in the castings using techniques developed previously. The pure metals examined (aluminium, copper, magnesium, zinc) all solidify by "skin formation" and approximate equations for the rate of skin thickening have been deduced. The solid-solution alloys (aluminium-10% magnesium, aluminium-5% zinc, copper-10% tin, copper-20% zinc, magnesium-10% aluminium) solidify in the "pasty" manner described previously for the aluminium-4% copper alloy. Two of the eutectiferous alloys studied (copper-10% aluminium and zinc-5% aluminium) solidify by "skin formation", but the mechanism of solidification of the others (aluminium-30% copper, aluminium-11% silicon, aluminium-13% silicon) is obscure, apparently approaching the "pasty" type. The observed solidification times of the castings were compared with those calculated from thermal data for the metal and mould, and, in most cases, reasonable agreement was found.

I.—INTRODUCTION.

PREVIOUS work¹ in which the solidification of sand castings in pure aluminium, aluminium-copper, and a few other alloys, was investigated by making temperature measurements in the castings, has shown that the constitution of the alloy exerts a profound influence on the mode of solidification of these materials. Sand-cast pure aluminium solidifies by what has been termed "skin formation", the casting consisting, at any instant during the solidification period, of a shell of completely solid metal enclosing a core of completely liquid metal; in contrast, an aluminium alloy containing 4% copper, and having a freezing range of about 100° C., forms a pasty mixture of liquid and solid with solidi-

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fication proceeding concurrently throughout the entire mass, freezing at the centre of the casting lagging slightly behind that at the surface. It was also found that the existence of a long freezing range is not always necessary for this pasty solidification to occur, a similar mode of solidification being observed in an aluminium-0.1% titanium alloy whose freezing range was only about 2° C. Short-freezing-range alloys of composition close to the eutectic presented a case of special difficulty. It was shown that during the solidification of an aluminium alloy containing 30% copper there existed a period during which large regions

TABLE I.—*Properties of Alloys Studied.*

Metal or Alloy	Liquidus Temperature, ° C.	Freezing Range, ° C.	Approx. Volume Latent Heat, cal./cm.*†	Approx. Thermal Conductivity, C.G.S. units	Approx. Proportion of Eutectic
Pure Aluminium *	660	Nil	242	0.48	Nil
Al-4% Cu *	650	102	248	0.3	0.04
Al-30% Cu *	560	12	268	?	0.88
Al-33% Cu .	548	Nil	268	?	1.00
Al-10% Mg .	615	165	238	0.2	0.08
Al-11% Si .	584 †	7 †	265	0.35	0.82
Al-13% Si .	600 †	23 †	298	0.35	0.96
Al-5% Zn .	650	10	240	0.4	Nil
Al-0.1% Ti *	662	2	242	0.3	Nil
Pure Copper .	1084	Nil	405	0.8	Nil
Cu-10% Al *	1037	Nil	380	0.1	§
Cu-10% Sn .	1015	217	381	0.1	0.15
Cu-20% Zn .	992	12	354	0.25	Nil
Pure Magnesium .	650	Nil	147	0.30	Nil
Mg-10% Al .	596	159	154	0.1	0.08
Pure Zinc .	419.5	Nil	164	0.24	Nil
Zn-5% Al .	382	Nil	169	0.2	1.00

* Studied in earlier work.¹

† Unmodified.

‡ Calculated from density of solid at melting point.

§ Nil in equilibrium, but apparently 1.00 when sand cast (see text, pp. 243-4).

of the casting were at the same temperature (the eutectic temperature), and since freezing was progressing inside these regions during the constant-temperature period it appeared that heat was being removed from the casting in the absence of a temperature gradient. The only tentative explanation which could be offered was that heat transfer was taking place by circulation of the liquid metal due to convection and gravity effects. On the other hand, a eutectic aluminium bronze solidified in a normal "skin-forming" manner.

The present work was carried out with the object of extending the

earlier work to a wider range of alloys to enable broad generalizations to be made. The mechanism by which a metal or alloy solidifies is most likely to be determined by the following physical properties: solidus temperature, freezing range and the proportion of eutectic present, volume latent heat, and thermal conductivity. The alloys studied were therefore selected so as to cover a wide range of these properties; details of the alloys are given in Table I. Some of the alloys studied in the earlier work have also been included in Table I for completeness. Secondary objectives were the measurement of the rate of "skin formation" (where this occurred) and the correlation of the solidification times of castings with times calculated by a modification of the method already described.¹

II.—EXPERIMENTAL TECHNIQUE.

1. Test Castings and Mould Materials.

Four types of castings were employed, and details of these are given below:

(1) A horizontal 5 in. dia. \times 10 in. cylinder run through the top at one end, as used in the earlier work.¹

(2) A vertical 5 in. dia. \times 10 in. cylinder. This casting was similar to that used previously,¹ but the method of moulding was different, the mould being made in three parts—a base, a cylindrical sleeve, and a top—as shown in Fig. 1.

(3) A vertical cylinder 5 in. dia. \times 6 in. long. This casting was designed with the object of securing approximately unidirectional solidification from the bottom upwards. The mould consisted of a sand base, and a cylindrical sleeve and a split top both made from plaster. The sleeve was heated in a muffle furnace to about the freezing temperature of the alloy being cast and was placed on the base immediately before pouring; this procedure was intended to minimize solidification from the side walls. The couples were placed in position

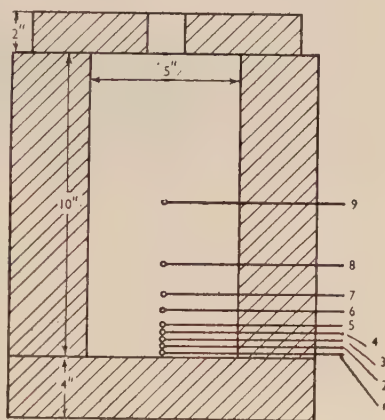


FIG. 1.—Details of Mould and Positions of Thermocouples in Vertical 5 in. dia. \times 10 in. Cylinder Casting.

and, after pouring, the preheated top was placed on the sleeve. Details of the arrangement are given in Fig. 2.

(4) A vertical slab casting, $18 \times 12 \times 2$ in. (Fig. 3). In this casting skin-formation rates were measured at the centre of one of the 18×12 in. faces.

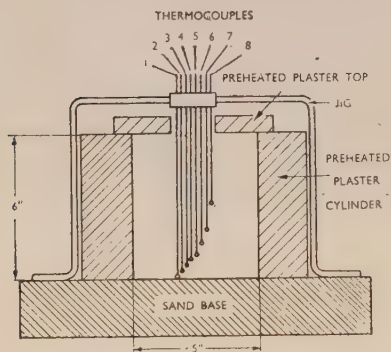


FIG. 2.—Details of Mould and Positions of Thermocouples in 5 in. dia. \times 6 in. Cylinder Casting. Thermocouples were arranged round the circumference of a $1\frac{1}{4}$ in. dia. cylinder concentric with the axis of the casting.

The moulds for the horizontal and vertical 5 in. dia. \times 10 in. long cylinders, the bases for the 5 in. dia. \times 6 in. vertical cylinders, and the moulds for the slabs were made in a synthetic sand consisting of Parish's No. 1 washed silica sand bonded with 5% bentonite. The grading of the sand is given below :

Sieve Fraction (B.S. Sieve Nos.)	Percentage
— 30 + 44	2.2
— 44 + 60	24.8
— 60 + 100	64.3
— 100 + 150	2.4

The moulds were dried before use for 3 hr. at 120°C . In order to prevent changes in the sand with use affecting the results, the sand was rejected after it had been used five times and was replaced with new material.

In experiments with reactive alloys mould reaction was prevented by adding to the sand either 6% sulphur (magnesium-base alloys) or 2% boric acid (aluminium-magnesium alloys). The aluminium-magnesium alloy castings were further inhibited by adding 0.025% beryllium to the metal.

2. Temperature-Measurement Technique.

As in the earlier work¹ the temperatures existing during solidification were measured with either 28 B. & S. gauge Chromel/Alumel

thermocouples (used for aluminium-, magnesium-, and zinc-base alloys), or with platinum/platinum-10% rhodium thermocouples (used for copper-base alloys). The thermocouples were protected along their lengths by twin-bore silica tubing; the exposed hot junctions were protected only by a thin wash of refractory cement. The thermo-

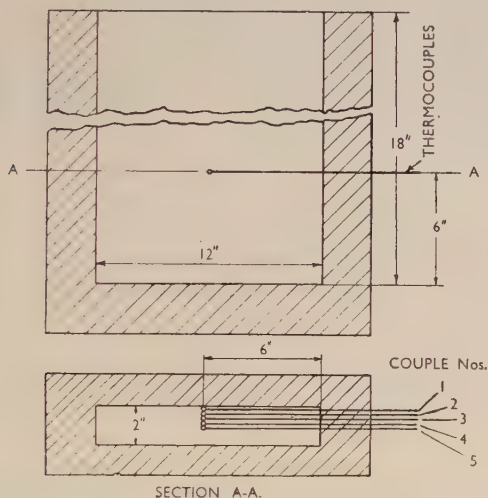


FIG. 3.—Details of Mould and Positions of Thermocouples in 18 × 12 × 2 in. Slab Casting.

couples were introduced into the moulds as shown in Figs. 1-3; in the case of the 5 in. dia. horizontal cylinders, the couples entered the mould cavity horizontally along radii and were arranged at the end of the casting opposite to the runner, much as in Fig. 1. For the reasons described previously¹ the thermocouples were generally used without prior calibration, but calibrated couples were employed where high absolute accuracy was required. The e.m.f. generated by the thermocouples were measured and recorded by the apparatus used in the earlier work.¹ The accuracy of measurement was about $\pm 0.5^\circ \text{C}$. in most cases, but for certain of the experiments this was increased to about $\pm 0.25^\circ \text{C}$.

3. Melting and Pouring.

The alloys used were prepared from the following materials :

Electrolytic copper	99.99% pure
Super-pure aluminium	99.99% pure
"Crown Special" zinc	99.99% pure
"Mellaneer" refined tin	99.8% pure
"Melpure" magnesium	99.9% pure

The pure metals and alloys were melted in Salamander or iron (for magnesium-base alloys) pots in gas-fired injector furnaces; the pure alloying element was added to the molten basis metal, except for aluminium-copper and aluminium-silicon alloys, when hardener alloys made from the above materials were employed. Each melt was heated to about 100° C. above the liquidus temperature of the alloy, degassed by an appropriate treatment, cooled to the casting temperature (100° C. superheat), and poured as rapidly as possible. When required, the aluminium-silicon alloys were modified by treatment at 760° C. with a flux consisting of two parts of sodium fluoride and one part of sodium chloride.

III.—RESULTS AND DISCUSSION.

The results obtained are reported under the headings: (1) Pure Metals, (2) Solid-Solution Alloys, and (3) Eutectic Alloys.

1. *Pure Metals.*

Cooling curves were obtained during the solidification of each of the three types of cylinder casting made in the four pure metals studied. In these experiments nine thermocouples were usually employed and these were placed at various distances from the metal/mould interface, being grouped most closely near the interface where solidification was most rapid and corresponded most nearly to unidirectional solidification. Representative sets of cooling curves are shown in Figs. 4 and 5. A set of curves for a similar aluminium cylinder has been given earlier.¹

It has always been assumed that pure metals normally solidify by "skin formation", and this is confirmed by the results of the present work. The fact that the temperatures recorded by calibrated thermocouples placed at the metal/mould interface fell past the freezing point without showing any measurable arrest, is clear proof of the occurrence of "skin formation". The behaviour of the interface couple was extremely sensitive to its position; provided it was in contact with the mould wall it behaved as described above, but if the couple bead was separated from the interface by more than a small fraction of a millimetre, undercooling followed by sharp recalescence and a short arrest was observed.

The kinetics of the solidification process in the castings were investigated by plotting the thickness, d , of metal solidified against the square root of the time, t , after casting, and thus evaluating the constants k and c in the equation:

$$d = k\sqrt{t} - c$$

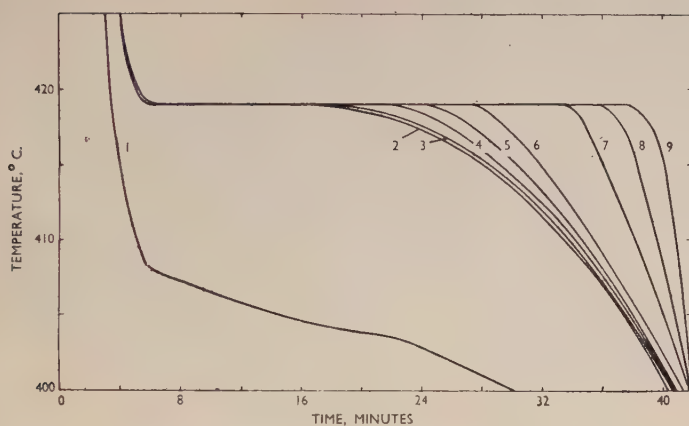


FIG. 4.—Temperatures in Horizontal 5 in. dia. \times 10 in. Zinc Cylinder.
Positions of Thermocouples.

1. Interface (metal side).	6. 1.1 in. from interface.
2. 0.17 in. from interface.	7. 2.1 " "
3. 0.37 " "	8. 3.0 " "
4. 0.52 " "	9. 4.8 " "
5. 0.75 " "	

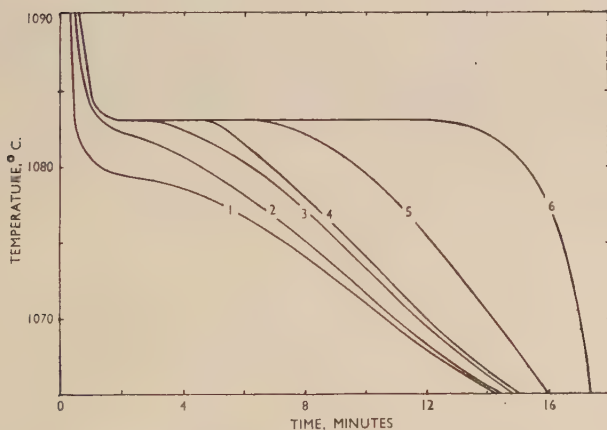


FIG. 5.—Temperatures in Horizontal 5 in. dia. \times 10 in. Copper Cylinder.
Positions of Thermocouples.

1. Interface (metal side).	4. 0.75 in. from interface.
2. 0.25 in. from interface.	5. 1.70 " "
3. 0.50 " "	6. 4.75 " "

The values of d and t were determined by observing the time at which the readings of successive thermocouples fell below the freezing point.¹ The values of the two constants obtained in this way from the different castings are given in Table II. In most cases the experimental points gave a straight line up to a distance of about an inch from the interface, diverging beyond this distance in the direction of higher values of d . In a few cases the points showed considerable scatter about the ideal straight line; possible reasons for this have been discussed in the earlier paper.¹ A number of specimen plots are reproduced in Fig. 6.

Table II shows that the values for the two constants obtained from the different castings in the same metal vary considerably; furthermore, all the values for k are greater (often considerably greater) than the theoretical maximum values given in the last column of Table II, which were calculated from the thermal properties of the metal * and from the

TABLE II.—*Approximate Values of Constants in Equation $d = k\sqrt{t} - c$ for the Solidification of Pure Metals and a Eutectic Alloy Cast with 100° C. Superheat.*

Units are inches and minutes.

Metal or Alloy	Form of Casting								Theoretical Max. Value of k
	5 in. dia. \times 10 in. Horizontal Cylinder		5 in. dia. \times 10 in. Vertical Cylinder		5 in. dia. \times 6 in. Vertical Cylinder		18 \times 12 \times 2 in. Vertical Slab		
	k	c	k	c	k	c	k	c	
Copper	0.50	0.33	1.2	2.1	1.1	1.4	0.27	0.18	0.24
Aluminium	0.4	1.30	0.5	0.8	0.5	2.5	0.26	0.29	0.23
Magnesium	0.7	0.6	2.0	2.5	0.8	0.8	0.50	0.65	0.36
Zinc	0.27	0.62	1.3	4.6	0.8 †	5.7 †	0.23	0.45	0.19
Cu-10% Al	0.4	0.48	1.2	2.2	1.0	2.8	0.27	0.27	0.25

† 150° C. Superheat.

known rate of heat extraction by the sand.^{2, 6} It seems clear, therefore, that, even in the centre of the 5 in. dia. plane mould wall, extraction of heat through the corners and cylindrical wall increases the rate of solidification, and that unidirectional solidification does not obtain. This is also true of the 5 in. dia. \times 6 in. long vertical cylinders despite pre-heating of the side walls. The reproducibility of these experiments on cylinders was on the whole poor, values of k obtained from replicate experiments often differing quite considerably.

Table II also shows that the rates of solidification in the vertical

* See ref. 4.

cylinders were higher than in the horizontal cylinders. The macrostructures of the castings suggest a possible explanation for this. Columnar macrostructures were invariably found in the horizontal cylinders (see, for instance, Fig. 16 (Plate I) of the previous paper¹), but in the vertical cylinders the macrostructures often showed regions of equi-axial crystallization near the base.

Fig. 12 (Plate XXXIV) is a particularly well-marked example of this. The occurrence of these equi-axial regions is not easy to understand, but it is tentatively suggested that they may have been caused by gravity segregation of free crystallites towards the bottom of the casting; such an effect would obviously increase the rate of solidification upwards from the base of the casting. In the case of the copper cylinders the fine equi-axial crystallization may have been due to oxygen absorbed during pouring. This dissolved oxygen might cause concentration gradients to form round the crystals at the mould walls and thus inhibit their further growth.³ This would result in the nucleation of free crystallites in the interior, which would tend to sink to

the bottom of the casting under the influence of gravity. The slower rates of solidification in the horizontal cylinders could be due to air-gap formation at the vertical plane ends of these castings, but the temperature records gave no indication of such an effect.

Examination of the macrostructure also revealed that the thermocouples in the 5 in. dia. \times 6 in. cylinders had in some instances interfered with the crystallization of the melt, producing a region of equi-

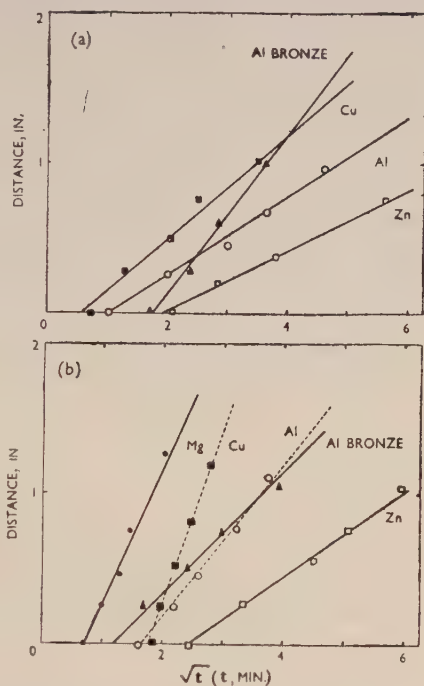


FIG. 6.—Rates of Skin Formation in Pure Aluminium, Copper, Magnesium, and Zinc, and 90 : 10 Aluminium Bronze, cast in (a) vertical slab moulds, and (b) horizontal (—) and vertical (----) cylinder moulds.

axial crystallization which was absent in similar cylinders made without any thermocouples in the mould cavity. This equi-axial crystallization might well increase the rate of solidification from the bottom of the cylinders upwards, as suggested above. Similar effects were noticed in 5 in. dia. \times 6 in. cylinders cast in other materials.

The cooling curves obtained from the slab castings were qualitatively similar to those from the cylinders, but, as Table II (columns 2, 4, 6, and 8) shows, the rates of skin formation in the slabs were consistently lower than in the cylinders. In contrast with the cylinder castings, the reproducibility of the skin-formation experiments with the slabs was fairly satisfactory and the linear relationship was found to hold good almost to the centre of the section. Furthermore, the values of k obtained from the slabs approach those calculated from the thermal properties of the mould much more closely than the k figures obtained from the cylinders; only in the case of magnesium does a substantial difference between the calculated and observed values exist, and in this instance the calculated rate may be in error since the latent heat of fusion of magnesium is not known accurately. It may therefore be concluded that unidirectional solidification is largely attained at the centre of the 18 \times 12 in. faces of the slabs and that the figures in columns 8 and 9 of Table II are approximate fundamental constants for the metal, pouring temperature, and mould material concerned. The value of k for aluminium (0.26 in./min.⁴) obtained from a slab casting agrees well with the figure of 0.28 in./min.⁵ found by Hunsicker,⁵ who used the "pour-out" method.

The foregoing considerations suggest that the skin-formation equations obtained from the work on cylinder castings have no fundamental significance. Nevertheless, these equations are important as indicating the sort of deviations from the ideal "skin-formation" rates which may be met with in castings of which the whole, or parts, consist of small cylinders, square sections, and the like. On the other hand, the skin-formation equations for the slab castings should apply with fair accuracy to the majority of castings (or parts of castings), whose section thickness is small in relation to their surface area.

The macrostructures of the slab castings were wholly columnar and there was no indication that the thermocouples had interfered with this columnar growth.

It was suggested earlier ¹ that in pure metals the solidification front advancing into the liquid metal might not be plane, but might consist of hills and valleys, the hills corresponding to the tips of the columnar crystals. In an effort to test this, a few 5 in. dia. \times 6 in. cylinders were made in which three thermocouples were placed at the same

distance from the mould wall. It was expected that, if the hill-and-valley theory were correct, freezing would be completed at the locations of these three couples at slightly different times. However, in all instances the readings of the three couples fell below the freezing point at the same time within the limits of experimental error. It was therefore concluded that if any irregularities were present in the solidification front, they were too small to be detected by the temperature-measurement technique.

2. Solid-Solution Alloys.

The cooling curves obtained from 5 in. dia. \times 10 in. cylinders in the four long-freezing-range alloys listed in Table I were all closely similar, as may be seen by comparing the typical examples in Figs. 7 and 8

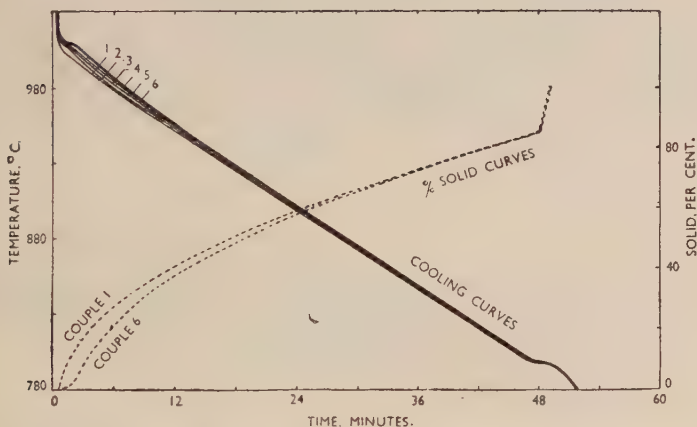


FIG. 7.—Temperatures in Horizontal 5 in. dia. \times 10 in. Cylinder in Copper-10% Tin Alloy.

Positions of Thermocouples.

- | | |
|-----------------------------|-----------------------------|
| 1. Interface (metal side). | 4. 0.75 in. from interface. |
| 2. 0.25 in. from interface. | 5. 1.0 " " |
| 3. 0.55 " " | 6. 1.55 " " |

with sets of similar curves given in the earlier paper ¹ for cylinders cast in the aluminium-4% copper alloy. It is clear that all the alloys have solidified in the pasty manner described there for the aluminium-4% copper alloy, freezing proceeding concurrently throughout the entire mass of metal, with solidification only a little more advanced at the surface than at the centre of the casting (see the percentage-solid curves in Figs. 7 and 8).

The results obtained with the various alloys differ principally in (a)

the magnitude of the temperature gradients present during solidification, and (b) the time to complete freezing. The temperature gradients present depend mainly on two factors: (i) the thermal conductivity of the metal, and (ii) the rate of heat abstraction by the mould. For example, in aluminium-4% copper alloy cylinders the gradient present soon after the beginning of solidification was about 2-3° C./in., while in aluminium-10% magnesium alloy cylinders (curves not reproduced) the corresponding gradient was about 5° C./in.; this difference is largely accounted for by the fact that the latter alloy has a lower conductivity. The corresponding gradient in the copper-10% tin alloy (Fig. 7) was about 6-8° C./in., and here the increased rate of heat

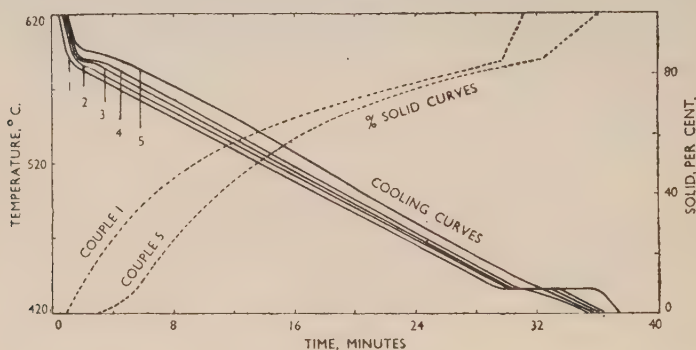


FIG. 8.—Temperatures in Horizontal 5 in. dia. \times 10 in. Cylinder in Magnesium-9.8% Aluminium Alloy.

Positions of Thermocouples.

- | | |
|----------------------------|-----------------------------|
| 1. Interface (metal side). | 4. 2.35 in. from interface. |
| 2. 0.7 in. from interface. | 5. 5.0 " " |
| 3. 1.4 " " | |

extraction by the mould at higher temperatures² is no doubt partly responsible for the steeper gradient, compared with the aluminium-4% copper alloy. The solidification times of the castings are discussed in Section III. 4.

Some of the magnesium-aluminium alloy cylinders were made from metal which had been superheated, but the cooling curves recorded were not appreciably different from those obtained from untreated metal.

Undercooling was observed at both the surface and centre of most of the copper- and aluminium-base alloys; this undercooling was generally about 2-3° C. at the surface and rather less at the centre. The magnesium alloy cylinders made from untreated melts had a grain-size of about 1 mm., while those from superheated melts had a grain-size of about 0.2 mm. No undercooling was detected in either case, suggest-

ing that both materials contained nuclei which facilitated crystallization of the solid solution.³

All the castings had equi-axial macrostructures and considerable amounts of intergranular porosity were present. This microporosity was generally coarse, particularly in the unrefined magnesium alloy castings. These, and to a lesser extent the aluminium-10% magnesium castings, showed a large number of long interdendritic fissures about 2 mm. wide, dispersed with their length approximately parallel to the isothermals in the casting during solidification. It is probable that

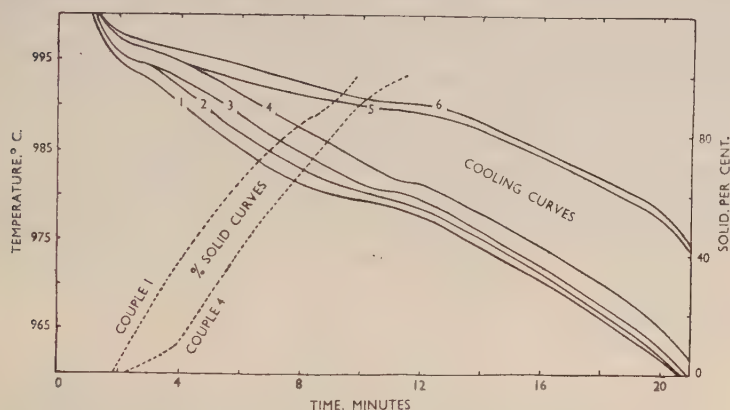


FIG. 9.—Temperatures in Horizontal 5 in. dia. \times 10 in. Cylinder in Copper-20% Zinc Alloy.

Positions of Thermocouples.

1. 0.1 in. from interface.	4. 1.1 in. from interface.
2. 0.45 " "	5. 4.2 " "
3. 0.65 " "	6. 5.35 " "

these fissures were due to mass movement of the pasty mixture of solid and liquid from the hotter towards the colder parts of the casting.

The work described above and in the earlier paper¹ suggests that all long-freezing-range alloys solidify in a "pasty" manner when sand cast, and that at no time during solidification do regions of wholly solid and wholly liquid metal coexist. It was thought, however, that castings in an alloy of shorter freezing range might show a completely solid outer shell separated from a fully liquid core by a pasty region. To test this suggestion, horizontal 5 in. dia. \times 10 in. cylinders were cast in two solid-solution alloys of short freezing range (10° – 20° C.); these alloys were an aluminium-5% zinc alloy and a copper-20% zinc alloy. Cooling curves for the casting in the latter alloy, given in Fig. 9 (note different

temperature scale), show that solidification had proceeded in a way similar to that obtaining in the castings in the long-freezing-range alloys. Results with the aluminium-5% zinc alloy were closely similar.

It seems likely that the factor determining whether skin formation or pasty solidification occurs in a given instance is the rate at which the mould abstracts heat from the casting; this factor controls the temperature gradients present during solidification and, when the temperature differences in a casting are of the same order as, or are smaller than, the total freezing range of the alloy, pasty solidification must result. Since the temperature gradients present during the solidification of sand castings are usually quite small, it is to be expected that solid-solution alloys will generally solidify in a pasty manner when sand cast. Pasty solidification is most likely to occur in fairly heavy sections where the average rate of heat abstraction is low; in thin sections which freeze rapidly while the mould is removing heat at comparatively high rates, a tendency towards skin formation is to be expected. Bearing in mind that the previous work ¹ has shown that an aluminium-0.1% titanium alloy, the freezing range of which is only 2° C.,* also solidifies in a pasty manner, when cast in a 5 in. dia. cylinder, it seems probable that sand castings of this size in solid-solution alloys (whose freezing points do not exceed about 1000° C.), rarely, if ever, solidify otherwise.

3. *Eutectic Alloys.*

The earlier work,¹ carried out with an aluminium alloy containing 30% copper, indicated that the mode of solidification of this eutectiferous alloy was different from that of a pure metal; a number of other eutectic alloys were investigated during the course of the present work in order to determine whether the effects observed with the aluminium-30% copper alloy were present during the solidification of eutectics in general.

The cooling curves obtained from cylinder castings made in the eutectic or near-eutectic alloys listed in Table I were found to fall into one of three categories; these are illustrated diagrammatically in Fig. 10 (a), (b), and (c). In all cases similar cooling curves were obtained from thermocouples placed at the centre of the casting, but the three types of record differ in the curves obtained from couples placed at or near the surface. In type (a) records the surface couple showed no arrest, the indicated temperature falling steadily and progressively past the eutectic temperature (undercooling and some recalescence were

* No data are available for the conductivity of the alloy, but it is probably relatively high and therefore favourable to skin formation.

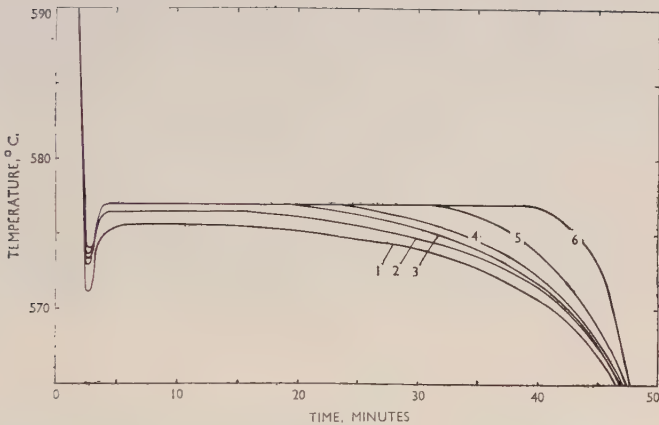


FIG. 11.—Temperatures in Horizontal 5 in. dia. \times 10 in. Cylinder in Aluminium-13% Silicon Alloy.

Positions of Thermocouples.

- | | |
|-----------------------------|-----------------------------|
| 1. Interface (metal side). | 4. 1.25 in. from interface. |
| 2. 0.38 in. from interface. | 5. 2.25 " " |
| 3. 0.72 " " | 6. 5.0 " " |

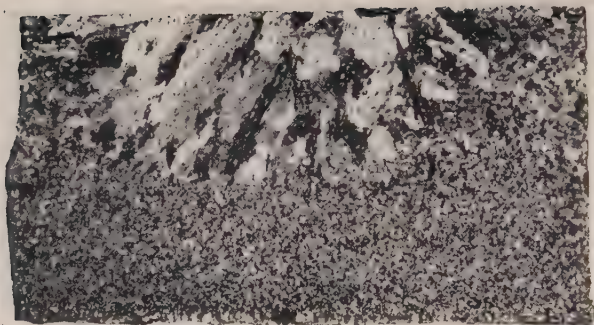
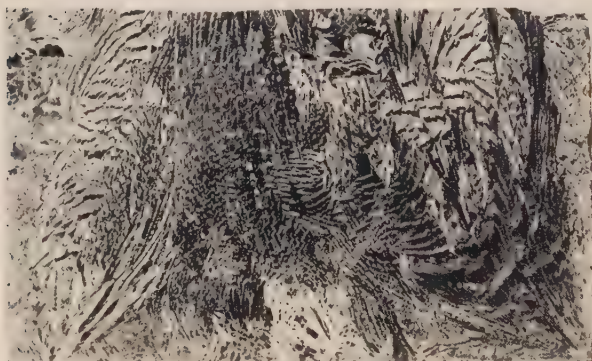


FIG. 12.—Vertical Section through Bottom End of a Vertically Cast 5 in. dia. \times 10 in. Copper Cylinder, showing fine-grained region at bottom of the casting. $\times \frac{1}{2}$.

(a)



(b)

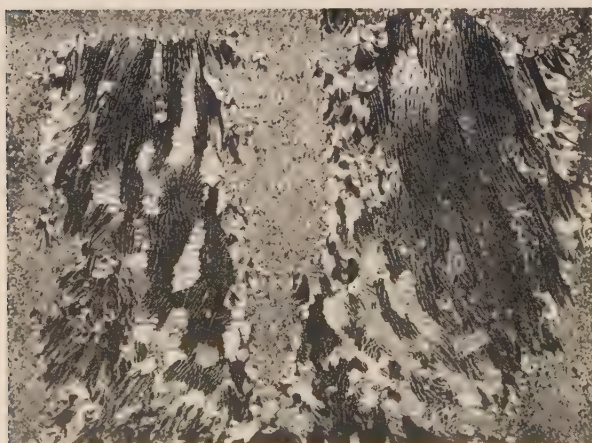


FIG. 13.—Vertical Sections through Bottom Ends of Vertically Cast 5 in. dia. \times 6 in. Cylinders in (a) Aluminium-33% Copper Alloy; (b) Zinc-5% Aluminium Alloy, showing Macrostructures. $\times \frac{1}{2}$.

sometimes observed). Records of this type indicate that skin formation has occurred. In type (b) records the surface temperature recalesced to the eutectic-arrest temperature * and then remained at this temperature for some minutes. This type of record was obtained in previous work with aluminium-30% copper alloy castings.¹ Type (c) was closely similar to type (b), differing only in that the surface couples did not show complete recalescence but rose to an arrest temperature somewhat below (1-2° C.) the eutectic-arrest temperature indicated by the other thermocouples. Records of this type are not necessarily inconsistent with skin formation, although it is hard to understand why the surface temperature should remain constant for so long. Owing to the smallness of the temperature differences, records of types (b) and (c) could only be distinguished by the use of calibrated thermocouples. Examples of records of types (a) and (b) have already been given (see Figs. 15 and 10, respectively, of the earlier paper¹). Fig. 11 (Plate XXXIII) is an example of a type (c) record.

Cylinder castings in 90:10 aluminium bronze invariably yielded records of type (a) (Fig. 15 of the earlier paper), and it was therefore concluded that this material solidifies by skin formation. Confirmation of this was obtained from a series of "pour-out" experiments in which

3 in. dia. \times 4 in. cylinders were overturned at various intervals of time after pouring. The liquid metal inside these castings was very fluid and poured out readily, leaving a smooth shell behind in the mould. Slab castings were also made in this alloy to determine the fundamental constants for the rate of skin formation; these are shown in Table II, together with constants obtained from the cylinder castings.

It is interesting to note that the 90:10 aluminium bronze (actual

* The accuracy of measurement was $\pm 0.25^\circ \text{C}$.

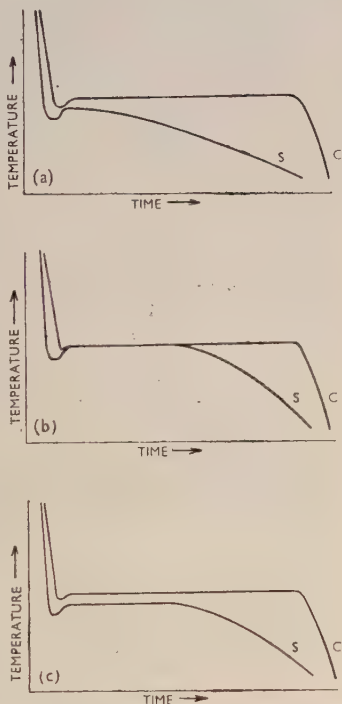


FIG. 10.—Types of Cooling Curves Obtained from Cylinder Castings in Eutectic Alloys.

S = Surface of casting.
C = Centre of casting.

composition 10.6% aluminium) solidifies wholly as a eutectic and shows no primary arrest, for this composition lies in the single-phase field to the right of the eutectic horizontal; under equilibrium conditions, it should therefore solidify as β instead of as $(\alpha + \beta)$ eutectic. Presumably, under non-equilibrium conditions the alloy undercools to the eutectic temperature, 1037° C. (or slightly below), when nuclei of α crystallize out preferentially and initiate eutectic crystallization.

Type (a) records were sometimes obtained from castings in the zinc-5% aluminium alloy, but types (b) and (c) were also observed. "Pour-out" experiments suggested that skin formation had occurred but, on plotting the thickness solidified (obtained from temperature measurements in slab castings) against the square root of the time, the expected linear relationship was not found, the plot showing considerable curvature, well outside the limits of experimental error. It appears, therefore, that even if this alloy generally solidifies by skin formation—and the temperature measurements suggest that this is not always the case—the mechanism is somewhat different from that exhibited by pure metals.

With the remaining eutectics studied—the aluminium-copper alloys (30 and 33%) and the aluminium-silicon alloys (11 and 13%)—records of types (b) or (c) were always obtained. Fig. 11 is an example of a type (c) record from a casting in the aluminium-13% silicon alloy. Modification did not cause any marked change in the records obtained from the aluminium-silicon alloys, the only apparent effect being depression of the eutectic temperature from 577° to 570° C. Micro-examination showed that the fluxing treatment employed had produced full modification of the structure. "Pour-out" experiments were performed on all these alloys, and only in one instance—with the modified aluminium-13% silicon alloy—was any evidence of skin formation obtained; with this alloy the metal poured out readily and appeared quite fluid but, in contrast with the aluminium bronze, the shells retained in the mould were of rather irregular thickness and had rough surfaces. With the other alloys the metal poured out of the 3 in. dia. cylinder 1½ min. after casting was very pasty and had to be shaken out of the moulds; 2 or 3 min. after casting it was impossible to pour any metal out, although the castings were not fully solid until about 9 min. after pouring.

It seemed unlikely that these effects could be accounted for by the separation from the melt of primary crystals before the beginning of eutectic solidification, because the quantities of primaries involved in no case exceeded a few per cent. As a result of the earlier work, which showed the apparent absence of temperature gradients during solidi-

fication in aluminium-30% copper alloy castings, it was tentatively suggested that heat transfer might be occurring as the result of movement of liquid and solid metal produced by gravity and convection effects. In an effort to check this suggestion, two horizontal 5 in. dia. cylinders were made in aluminium-30% copper alloy, with the thermocouple tips placed inside a 1 in. dia. tube made from perforated steel sheet ($\frac{1}{2}$ mm. thick); this tube was concentric with the longitudinal axis of the cylinder. It was thought that the presence of this screen would prevent any motion of the semi-liquid metal in the neighbourhood of the thermocouple tips; a temperature record of type (a) should therefore be obtained, if the suggestion previously advanced was correct. The results were inconclusive, a type (a) record being obtained in one instance and a type (b) in the other. However, it may be significant that this is the only occasion on which a type (a) record was obtained with the aluminium-30% copper alloy.

The macrostructures of the eutectic alloy castings were difficult to interpret. In most cases the structures, in some parts of the castings, were suggestive of columnar growth towards the heat centre of the casting. Typical examples are shown in Figs. 13 (a) and (b) (Plate XXXIV). At the higher magnifications the roughly parallel streaks seen in Fig. 13 seemed to be long rods or plates from which the lamellar eutectic growth had proceeded, and the appearance of Fig. 13 (a), for example, might be explained by assuming that the long and slender eutectic grains had toppled over or bent during freezing. Such effects, combined with convection effects, might be responsible for the cooling curves of types (b) and (c).

While it cannot be claimed that these further observations provide an adequate picture of the mode of solidification of eutectic alloys, the results are not inconsistent with the view that motion of solid and liquid metal occurs during solidification of some of the alloys.

4. *Solidification Times of Castings.*

In the previous work,¹ the solidification times of a number of aluminium and aluminium alloy cylinders were compared with figures calculated from the thermal properties of the mould. Fairly good agreement was found for the alloy cylinders, but the observed solidification times of the pure aluminium cylinders were considerably shorter than those predicted. The explanation advanced for this was that the calculations were in error owing to their neglect of corners and mould curvature; apparent good agreement was found in the case of the alloy cylinders, because sinking of the top surfaces of the casting away from

the mould had reduced the rate of heat extraction and had counteracted the error inherent in the calculations.

A recent experimental investigation ⁶ of the heat extraction at the corners of moulds and at curved mould surfaces has enabled corrections to be made for these effects. The solidification times of the cylinder casting studied in the present work were computed using the modified method, and the results of these calculations are given in Table III, together with the observed freezing times; observed and recalculated times for some of the castings studied earlier ¹ are also included for completeness. The data used in making the calculations was taken from the review of literature ⁴ (thermal properties of the metals), and from another paper by one of the present authors ⁶ (thermal properties of the mould).*

Table III shows that the calculated freezing times of most of the pure metal castings agree with the observed times within about 10%, an accuracy which is probably as good as can be hoped for in these calculations since the thermal data are not known precisely. The only pure metal castings for which the error exceeds 25% are two of the magnesium castings—this large discrepancy may be due to the fact that the relevant thermal constants of magnesium have not been determined accurately—and two of the copper castings.

As was to be expected, the observed solidification times of many of the long-freezing-range alloys were greater than those calculated; this is no doubt caused by sinking of the upper part of the casting as described above. On the other hand, the calculated times for the two castings made in solid-solution alloys of short freezing range agree fairly well with those observed, and it is significant that little sinking of the upper parts of these castings was noted.

The observed solidification times of the eutectic alloys are on the whole in good agreement with those calculated; the fact that most of the observed times are slightly greater than those calculated is readily accounted for by the irregular pipes which formed on the top surfaces of the castings. It is less easy to explain why the observed times were in a few cases smaller than those calculated; however, except in one instance, the differences are small and probably within the limits of experimental error.

The agreement found between the observed and calculated solidification times is, on the whole, quite satisfactory in view of the unreliability of some of the thermal data used and of the unpredicted shrinkage and

* The values of the mould constant used in the calculations were 107 cal./cm.²/min.^½ at 548° C. and 260 cal./cm.²/min.^½ at 1083° C.; intermediate values were obtained by interpolation.

TABLE III.—*Solidification Times.*

Type	Metal or Alloy	Form of Casting					
		5 in. dia. × 10 in. Horizontal Cylinder		5 in. dia. × 10 in. Vertical Cylinder		18 × 12 × 2 in. Vertical Slab	
		Experi- mental Solidi- fication Time, min.	Cal- culated Solidi- fication Time, min.	Experi- mental Solidi- fication Time, min.	Cal- culated Solidi- fication Time, min.	Experi- mental Solidi- fication Time, min.	Cal- culated Solidi- fication Time, min.
Pure Metals	Zinc	38	36	38	34	31	29
	Magnesium	14.0	11.4	11.5	11.4	5.4	8.4
	Aluminium	26 † <i>a</i>	23	25	21	21	19
	Copper	14.0	18	14.5	18	11.5	12.8
Long-Freez- ing-Range Solid-Solu- tion Alloys	Al-4% Cu	62 * † <i>b</i>	33	60 *	31
	Al-10% Mg	51	49	65 *	38
	Mg-10% Al	36	31	36	29
	Cu-10% Sn	49 *	36	39 *	29
Short-Freez- ing-Range, Solid-Solu- tion Alloys	Al-5% Zn	23	22
	Cu-20% Zn	19	16
Eutectic Alloys	Zn-5% Al	47	47	47	44
	Al-30% Cu	42	39	48	39
	Al-11% Si	35	42	40	34
	Modified Al-11% Si	40	42	44	40
	Al-13% Si	60 *	40
	Modified Al-13% Si	48	47
	Cu-10% Al	16	17	15.5	16	14	11.5

* Upper surface of casting not in contact with mould.

† Casting made in previous work.¹ *a* Mean of six determinations. *b* Mean of three determinations.

piping effects due to the fact that the castings were unfed. The results obtained suggest that it should be possible to calculate with reasonable confidence the freezing times of fed castings which are not too complex in shape; it would not seem too much to hope for an accuracy of about $\pm 15\%$.

The freezing time of a casting is dependent upon (i) the heat content of the casting above the solidus temperature, and (ii) the rate at which the mould extracts heat. The influence of these two factors is well shown by comparison of the figures given in Table III with the thermal properties in Table I. Thus, despite the fact that the heat contents of the copper-base castings are greater than those of the aluminium-base castings by a factor of about 1.5, the solidification times of the copper-base castings are shorter, because at the freezing point of copper the mould removes heat about 2.75 times faster than at the temperature at which aluminium alloys solidify.² Although magnesium-base alloys have freezing temperatures similar to those of aluminium-base alloys, castings in the former solidify faster, because their heat capacities are

only about three-fifths those of the corresponding aluminium castings. The aluminium-10% magnesium and magnesium-10% aluminium castings show this effect particularly well, for these materials have almost identical freezing ranges and temperatures.

IV.—SUMMARY AND CONCLUSIONS.

The results of the work described in this paper and the conclusions reached are briefly summarized below :

(1) The pure metals copper, aluminium, magnesium, and zinc solidify by skin formation. Approximate equations for the rates of skin formation of these materials under conditions of unidirectional solidification have been determined experimentally. In practice the rates of skin formation in sand castings are likely to be much higher, except near the centres of flat surfaces of large castings.

(2) Alloys with long freezing ranges solidify in the "pasty" manner described in an earlier paper. The present work suggests that nearly all sand-cast solid-solution alloys, even those of short freezing range, solidify in this way, especially when cast in heavy sections.

(3) The mode of solidification of eutectic alloys remains obscure. In some cases skin formation or a near approach occurs; in others some form of pasty solidification seems to obtain.

(4) The solidification times of castings can be computed with fair accuracy using a modified method of calculation described in another paper. This method should yield reasonably accurate results with castings of simple shape.

ACKNOWLEDGEMENTS.

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SOME OBSERVATIONS ON THE α - β TRANS-1279 FORMATION IN TITANIUM.*

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SYNOPSIS.

The α - β transformation has been studied in titanium prepared both by the van Arkel iodide process and by magnesium reduction. A new method, involving observations on the changes of hydrogen equilibrium pressure with temperature in very dilute solutions of hydrogen in the metal, has been used. It has been found that whereas the transformation in the van Arkel material occurs sharply at a single temperature, that in the magnesium-reduced material takes place gradually over a temperature range of some 100° C.

Resistance measurements carried out on the materials illustrate the same point. A marked flattening of the resistance/temperature curves in both the α and β phases has been observed as the transformation is approached. An explanation has been suggested for the negative temperature coefficient of resistivity of β -titanium recently described by Greiner and Ellis (*Trans. Amer. Inst. Min. Met. Eng.*, 1949, **180**, 657).

I.—INTRODUCTION.

EARLY investigators¹ of the properties of titanium metal established the fact that it underwent a phase transformation at a temperature stated to be 880° \pm 20° C. During recent studies of the titanium-hydrogen system,² the author has obtained by thermodynamic calculation the figure 882.2° \pm 0.5° C. for titanium prepared by the van Arkel iodide process,³ this being the purest material yet made. The method is, however, slow and expensive, and by far the greater part of the titanium now available is made by a process originally suggested by Kroll,⁴ in which titanium tetrachloride is reduced by magnesium. The metal produced by this method is ductile, but contains both gaseous and metallic impurities amounting to more than 1 at.-%. As a result of the interest aroused by the practical possibilities of titanium, Kroll material is now being used in many investigations on the properties of the metal. The effect of impurities in titanium metal is known to be great, and it is necessary both from the practical and theoretical viewpoints to ascertain the extent of the effect on the transformation, of the impurities contained in the Kroll material. The transformation in both the van Arkel and the Kroll material has, therefore, been studied by a method depending on the change which occurs on transformation in

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the equilibrium pressure of hydrogen in very dilute solutions in the metal.

Among recent publications concerning the Kroll material is an American report ⁵ in which it is stated that the temperature coefficient of resistivity in β -titanium is negative. This is a surprising result and is not in agreement with the early work of de Boer, Burgers, and East.¹ The resistance changes occurring in the temperature range which includes the transformation have, therefore, also been studied for both the van Arkel and the Kroll material and the results correlated with those obtained by the hydrogen equilibrium-pressure method. An explanation of the American results is suggested.

The van Arkel titanium used was prepared by Philips' Gloeilampenfabrieken, Eindhoven, and the Kroll material by the U.S. Bureau of Mines.

II.—THE HYDROGEN EQUILIBRIUM-PRESSURE METHOD.

In studying the titanium-hydrogen system it was found that the α - β transformation could be followed by observing changes in the pressure of hydrogen in equilibrium with the alloys in a closed system. It was also found that, even when the amount of hydrogen in the system was reduced until the hydrogen content of the metal was of the order of 0.05 at.-%, the changes in equilibrium pressure with temperature were quite measurable, and the transformation manifested itself as a marked discontinuity on a curve in which the reciprocal of the absolute temperature was plotted against the logarithm of the equilibrium pressure. This suggested a means of studying the transformation. The effect of this quantity of hydrogen on the transformation temperature of the pure metal has been calculated from the results obtained in the study of the titanium-hydrogen system and found to be less than 0.3° C.; it can therefore be expected to be of the same order of magnitude as the effect of other impurities in the metal, which even for the van Arkel material amount to 0.07 at.-%. The transformation process studied by this method is not, therefore, significantly different from that of metal in which no hydrogen is present.

Fig. 1 is a diagrammatic representation of the apparatus used for the determination of hydrogen-pressure/temperature curves. The alloy specimen, in the form of a block weighing about 0.5 g., is placed in the silica tube *A* which is heated by furnace *B*. *C* is a Pirani gauge with an internal volume of about 1 c.c. and consists of the filament of a 6.3 V. panel bulb. The stability and sensitivity of this type of gauge was found to be completely satisfactory over the range of pressures (of the order of 10^{-3} - 10^{-4} mm. Hg) covered during the experiments. The

internal volume of the specimen tube, which must be small in order that the amount of hydrogen necessary to create the equilibrium pressure remains a negligible fraction of the hydrogen dissolved in the metal, is reduced by inserting a silica rod along the length of the specimen tube. Tap *D* allows the specimen and gauge to be isolated from the remainder of the apparatus when pressure/temperature measurements are being made.

Before beginning the experiment the apparatus is evacuated to a pressure of 10^{-5} mm. Hg and the specimen-tube carefully outgassed. The pure hydrogen to be dissolved in the specimen is generated by

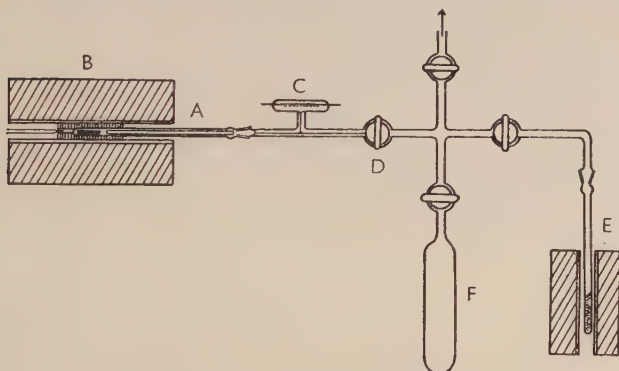


FIG. 1.—Apparatus Used for Determination of Hydrogen Equilibrium-Pressure/Temperature Curves.

heating titanium hydride which is contained in tube *E*. The hydrogen is collected in a bulb of known volume, *F*. The pressure in the bulb is so arranged that when the hydrogen is admitted to the specimen tube, the concentration of hydrogen in the specimen is 0.05 at.-%. The same hydrogen concentration was used for all the experiments.

The temperature of the specimen-tube furnace was controlled to within $\pm 0.5^\circ$ C. Equilibrium hydrogen pressures were measured over the temperature range 800° – 980° C. for both van Arkel and Kroll material. It was found that equilibrium pressures for any given temperature were established almost instantaneously, except in the temperature range in which the transformation was actually occurring, when times of up to 2 hr. were required before equilibrium was attained. Identical curves were obtained both on heating and cooling.

The logarithm of the equilibrium hydrogen pressure plotted against the reciprocal of the absolute temperature for the van Arkel material

is shown by the full line in Fig. 2. It can be seen that the pressure/reciprocal temperature curve is linear up to 882.5°C ., indicating that there is no change of heat of solution of hydrogen in α -titanium with temperature. Above 930°C . the relationship again becomes linear, but the slope of the curve now corresponds to the heat of solution of hydrogen in β -titanium. For a pure material, it would be expected that at the transformation temperature the pressure would change isothermally from the value indicated by the α -titanium curve to that corresponding to the β -titanium curve. From Fig. 2 it can be seen that

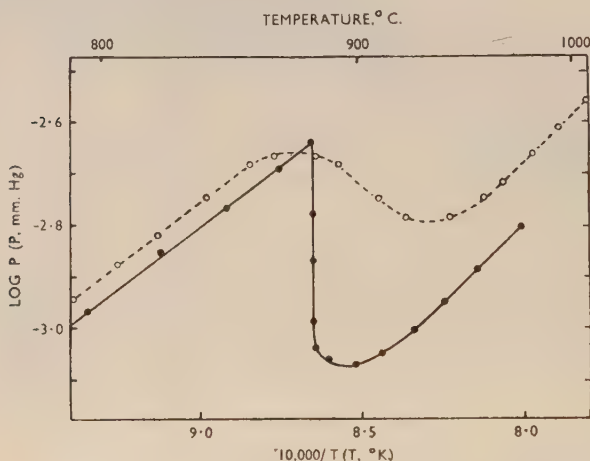


FIG. 2.—Hydrogen Pressure as Function of Reciprocal Temperature for Titanium Containing 0.05 at.-% Hydrogen.

● — van Arkel titanium.
○ --- Kroll titanium.

as the $\alpha \rightarrow \beta$ transformation begins, the expected isothermal pressure change does in fact occur. The equilibrium pressure at the transformation temperature does not, however, reach the value which would be expected from the extrapolation of the linear portion of the pressure/temperature curve of β -titanium but remains somewhat above it. On increasing the temperature, the pressure values approach the extrapolated curve gradually, and finally join it at 930°C . From this it may be concluded that the greater part of the material is transforming at $882.5^\circ \pm 1.0^\circ\text{C}$. The remaining material is apparently transforming gradually over a range of higher temperatures up to 930°C .

It is known that the presence of oxygen in titanium increases the transformation temperature. Since the dissociation pressures of

solutions of oxygen in titanium are considerably below 10^{-6} mm. Hg, some contamination of the specimen by oxygen during the experiment is inevitable. The rate of diffusion of oxygen in titanium is, however, slow, and the contamination occurring during a normal experiment will therefore be confined to the surface layers of the specimen, leaving the bulk of the specimen oxygen-free. This would explain the form of the curve obtained. Furthermore, it has been found that deliberate additions of oxygen to the specimen do not affect the sharpness of the initial drop of equilibrium pressure at the transformation temperature or the temperature at which this drop occurs, but cause a

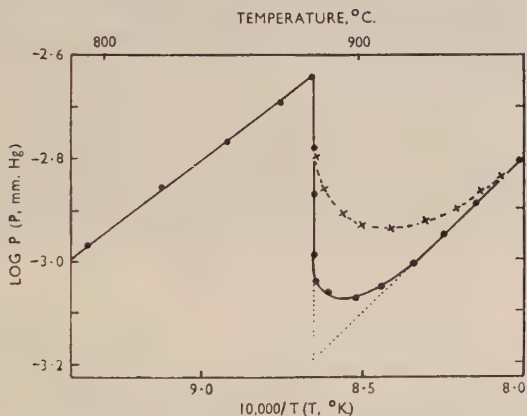


FIG. 3.—Effect of Superficial Oxidation of van Arkel Titanium Specimen on Equilibrium-Pressure/Reciprocal-Temperature Curve.

- Theoretical behaviour of uncontaminated specimen.
- Normal experimental curve.
- Deliberately contaminated specimen.

greater departure from ideal behaviour at the completion of the transformation, as is shown in Fig. 3, where the full line is the pressure/reciprocal-temperature curve for van Arkel material to which no oxygen has been deliberately added and the broken line is that for a similar specimen which has been superficially oxidized. The transformation temperature, $882.5^{\circ} \pm 1^{\circ} \text{C.}$, may be taken as that of oxygen-free material.

Analysis of the Kroll material gives : O 0.35, C 0.40, N 0.14, Si 0.07, Mg 0.25, Fe 0.17, Mn 0.02, Co 0.02 at.-%. The extent to which its behaviour departs from that of the purer van Arkel metal may be determined by examination of its equilibrium-pressure/temperature curve shown by the broken line in Fig. 2. At temperatures up to 850°C. ,

the curve for the magnesium-reduced material is linear and parallel to that of the van Arkel material. It lies, however, slightly above it, the impurities present in the lattice evidently making the entry of hydrogen atoms more difficult. The magnesium-reduced specimen begins to transform at 850°C. , where the curve first departs from the linear. Between 850° and 955°C. , at which temperature the curve again becomes linear, the material is in the two-phase condition. The linear part of the curve above 955°C. , which corresponds to the β -region, again lies parallel to that of the van Arkel material and slightly above it. From the wide temperature range over which the transformation takes place it is evident that the effect of the impurities is severe and that no conclusions regarding the equilibrium behaviour of pure titanium can safely be drawn from experiments in which Kroll material is used.

III.—RESISTANCE CHANGES IN α - AND β -TITANIUM.

An example of the error into which investigators may be led by the use of magnesium-reduced titanium is to be found in the work, mentioned earlier, of Greiner and Ellis ⁵ on the resistivity of titanium, in which it was found that β -titanium had a negative coefficient of resistivity.

Resistance measurements have been made by the present author on both van Arkel and magnesium-reduced titanium. The specimen was in the form of rolled strip, 0.008 in. thick, $\frac{1}{4}$ in. wide, and about $2\frac{1}{2}$ in. long, held in screw clamps made of titanium. Titanium wire potential leads were attached to the strip at a distance of 2 in. apart. The use of titanium alone for the electrical connections to the specimen prevented its contamination by other metals. The specimen was surrounded by a titanium sheath to absorb any gas entering the system, and the whole assembly enclosed in a clear silica tube which was evacuated to a pressure of 10^{-5} mm. Hg. As an additional precaution against the entry of oxygen and nitrogen into the system, the silica tube was contained in an outer envelope of silica evacuated to a pressure of 10^{-3} mm. Hg before inserting it in a tube furnace. The change in resistance of the specimen with temperature was determined by comparing the specimen resistance with that of a standard resistance by the usual potentiometric method. As in the case of the measurement of hydrogen equilibrium pressures, the temperature of the specimen, measured by a platinum/platinum-rhodium thermocouple placed in close proximity to the specimen, was maintained to within $\pm 0.5^{\circ}\text{C.}$ of any desired temperature. In the temperature range in which the specimens were undergoing a transformation it was found necessary to maintain the

specimen at each temperature for long periods before a constant value of the resistance could be obtained.

The anisotropy of thermal expansion in hexagonal titanium causes a slight change in dimensions of the strip specimens on heating or cooling, and it is not possible, when using this type of specimen, to give accurate values of the change of resistivity of the material with temperature.

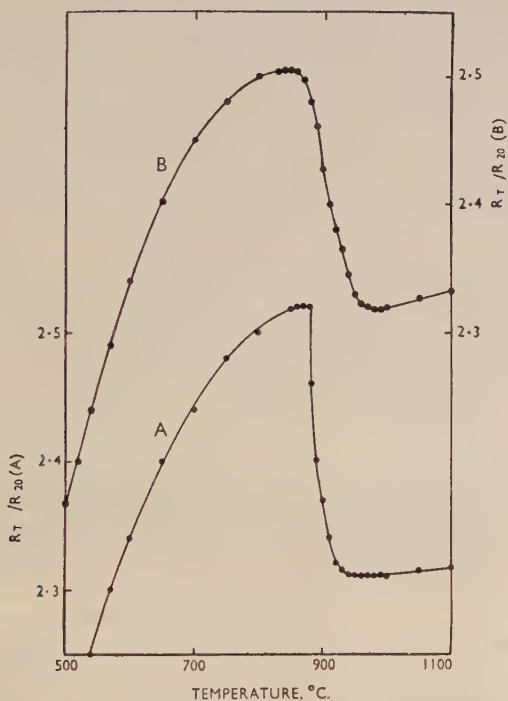


FIG. 4.—Ratio of Resistance R_T at Temperature T to Resistance R_{20} as Function of Temperature for van Arkel (curve A) and Kroll (curve B) Titanium. For clarity the curves are shown displaced vertically.

The results have, therefore, been presented as the ratio between the specimen resistance at any given temperature and the resistance of the same specimen at 20°C . At the latter temperature, the resistivity of the van Arkel titanium was 42.1×10^{-6} ohm-cm., while for the Kroll material a value of 55.6×10^{-6} ohm-cm. was obtained.

The results obtained for the van Arkel and the Kroll metal are shown in Fig. 4, in which the change in resistance is plotted against temperature for the two materials. It will be seen that there is a

marked similarity between the form of these curves and those of the equilibrium-pressure/temperature curves. For the pure material there is a sharp fall in the resistance at 882° C. and again part of the specimen transforms at a higher temperature, the transformation being complete at 940° C. Above this temperature the resistance curve is that of the pure β material and the change of resistance with temperature, although small, is undoubtedly positive.

It would appear from the curve that a greater portion of the specimen is transforming at temperatures above the true transformation temperature than in the previous experiment. Since the surface area of the strip used for the resistance measurements is much greater in relation to its volume than that of the block specimen used for the hydrogen-pressure work, the amount of oxygen contamination occurring during the experiment may well be greater in this case. There is, however, another possible contributory cause for the observed form of the curve. Volume changes occurring during the transformation cause the surface of the strip to buckle, and, by changing its shape, tend to increase the resistance of the strip even though its resistivity is unchanged. This would have the effect of increasing the rounding off of the resistance curve as the transformation proceeds. Once the transformation is complete no further buckling takes place, and the temperature coefficient of resistivity of the β material may be estimated from the curve, although it is not possible to determine the absolute resistivity.

The resistance/temperature curve for the Kroll material again shows the transformation to occur over the temperature range 860°–960° C. Once the transformation is complete, the resistance of the specimen begins to increase, indicating again that the temperature coefficient of resistivity of the β form is positive. The experimental points obtained by Greiner and Ellis on similar material have been found to lie on the same curve as that obtained in the present work. The small number of their points, however, appears to have led them to misinterpret their results, and to infer the existence of a sharp transformation point (fixed by extrapolation at 882° C.) at that part of the curve where the formation of the β phase has progressed sufficiently to cause the curve to begin to turn downward. The downward-sloping part of the curve corresponding to the ($\alpha + \beta$) region has, in fact, been taken by these workers to be the curve for the pure β phase, which they therefore concluded to have a negative temperature coefficient of resistivity. A note by other workers⁶ also mentions a negative coefficient of resistivity for β -titanium. The type of material used for the experiment is not mentioned and few details of the results are given. It is not possible, therefore, to discuss them critically.

CONCLUSIONS.

This work illustrates the difficulties involved in the accurate determination of the properties of pure titanium. It has been found that, even when the purest material available is used, it is not possible completely to prevent surface oxidation of the specimen in spite of careful experimental methods. It has also been shown that the effects of impurities present in titanium produced by the magnesium reduction of the tetrachloride are sufficiently great to cause the α - β transformation to occur over a temperature range of about 100° C. instead of at a fixed temperature. It is probable that other phase changes occurring in titanium-base alloys will be similarly affected. It would not, therefore, be expected that systems in which Kroll titanium is alloyed with another metal would necessarily obey the rules for binary alloy systems.

ACKNOWLEDGEMENTS.

The work presented in this paper forms part of the programme on the properties of titanium and its alloys being carried out by the Physical Metallurgy Section of the Australian Commonwealth Scientific and Industrial Research Organization, under the general direction of Professor J. Neill Greenwood, in the Baillieu Laboratory, University of Melbourne. The author expresses his indebtedness to his colleagues, and especially to Mr. H. W. Worner, who has been examining the effect of the α - β transformation on other physical properties of titanium, for many valuable discussions during the period in which this work was carried out.

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REVIEW OF PUBLISHED INFORMATION ON 1280 THE OXIDATION AND SCALING OF COPPER AND COPPER-BASE ALLOYS.*†

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

Part I of the review describes methods used in experimental work on the oxidation of metals, including weighing, optical and electrolytic methods for measurement of oxidation rates, and X-ray and electron-diffraction methods for the study of oxide-film structures.

The rate of oxidation of copper and the structure of the films formed are considered in Part II. There is a reasonably good agreement on the oxidation rate/temperature characteristic for copper, the logarithm of oxidation rate/reciprocal of absolute temperature curve consisting of two straight lines of different slopes intersecting at about 600° C.

In Part III are reviewed the influence of alloying elements on the oxidation of copper and some effects of variations in the oxidizing atmosphere. A comprehensive table incorporates references to all the work found dealing with the oxidation of copper-base alloys. Selective oxidation and subscale formation are included in this section and modern theories on oxidation phenomena are also discussed.

Part IV deals with the practical aspects of oxidation, with particular reference to the adherence of troublesome scales. Little has been published about the scaling characteristics of copper and copper-base alloys at normal processing temperatures, and slight information is available on the effects of impurities in bright-annealing atmospheres.

INTRODUCTION.

A NUMBER of reviews covering the oxidation and scaling of metals have been published, one of which was issued by the Department of Scientific and Industrial Research ¹ in 1935 and one more recently by Lustman ² in 1946. In 1940 Vernon ³ reviewed recent studies on thin oxidation films, and Mott ⁴ contributed a paper on the mechanism of oxidation. The theories of Wagner and his co-workers were considered by Price ⁵ in 1937. Mention must also be made of Dr. U. R. Evans's book ⁶ in which much information is to be found on this subject. These reviews and many of the original papers have been consulted in preparing the present review of available information.

Part I describes experimental techniques used in the study of oxidation of metals and alloys. Part II is a summary of information

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on the oxidation of copper and includes reference to the mechanism of oxidation, the constitution and structure of the oxide film, and the effects of temperature, time, oxygen concentration, &c., on the rate of growth and type of oxide formed. The effect of alloying elements on the oxidation of copper and the effect of variations in the oxidizing atmosphere are considered in Part III, selective oxidation and internal oxidation and subscale formation being included. Some practical aspects of the oxidation of copper and copper alloys, such as scale thickness, adherence, and the prevention of scaling by the use of neutral or reducing atmospheres, are outlined in Part IV.

I.—METHODS OF IDENTIFICATION OF OXIDE FILMS AND MEASUREMENT OF FILM THICKNESS AND RATE OF OXIDATION.

One of the earliest and probably most commonly used means of determining oxidation rate, and therefore film thickness, is the gravimetric method. By this method, either continuous measurement of the increase in weight may be made with the aid of a special balance or calibrated silica spring ⁷ or the specimen may be removed from the oxidation furnace (together with any loose scale), and the increase in weight measured. In some cases the loss in weight is recorded on removal of the scale.

Recently improvements have been made in gravimetric technique by Dumez ⁸ who adapted the normal type of chemical balance to the automatic recording of oxidation curves at constant and varying temperatures. Chevenard ⁹ has designed a special balance employing a quartz or Invar beam with a fine-wire suspension, also with automatic recording. Both Dumez and Chevenard have placed the furnace above the balance in order to reduce the amount by which the heat from the furnace disturbs the operation of the balance. Continuous measurement reduces errors due to exfoliation of scale on cooling, permits the detection of small changes in oxidation rate due to film cracking, and facilitates repetition.

The above methods are generally used for the thicker films and exfoliating scales, but suffer from inherent inaccuracies when applied to thin films. It is in this sphere that the greatest progress has been made in the last decade. The electron-diffraction camera has been employed by many investigators, and two techniques have been developed: (i) The film may be examined *in situ* on the metal, whereupon information regarding its structure and composition may be obtained from diffraction data. The electron-diffraction patterns are produced by the surface layers, some 100–300 Å. thick; no information is afforded about the structure of the interior of thicker films, and films of less

than about 100 Å. may exist without detection. (ii) Alternatively, the film may be stripped by chemical means and examined by transmission. This method can be used for films thinner than about 500 Å., but its value is doubtful owing to the possibility of changes in the structure of the films due to removal from the metal base. No reliable indication of film thickness can be obtained either by electron diffraction or transmission.

Many workers have used one of the optical methods^{10, 11, 12, 13} which involve the reflection of polarized light. At least one of the methods available is applicable to films less than 50 Å. in thickness. Lustman and Mehl¹¹ have recently employed an optical method in their investigation of the oxidation of single crystals of copper. This involves the use of polarized monochromatic light obtained from a mercury-vapour lamp. The refractive index and thickness of the film on copper may be determined by comparing the measured change in ellipticity with the theoretical relationship determined by Leberknight and Lustman.¹⁴ The range of thickness covered in the investigations of Lustman and Mehl¹¹ was from 0 to 1600 Å., and an accuracy in measurement of 1-5% is claimed. The main disadvantage of this method is that the film constants have to be determined for the oxide (or sulphide) present, and that it gives a reliable result only when the film consists of crystals of a single oxide or sulphide of known structure.

The standard of accuracy in the measurement of film thickness by the optical method described above is far greater than that obtained in the temper-colour method, which consists of a comparison of the interference colours formed by the film with some standard, and which is not applicable to films less than about 400 Å. in thickness.

The electrolytic method^{15, 16} requires that the time be observed for the cathodic reduction of each part of the film substance. The film thickness may be determined from the quantity of electricity required for this reduction. Some knowledge of the expected film composition is necessary, but, for example, in the case of copper it is possible to obtain the thickness of each component of the film, whether CuO, Cu₂O, or sulphide. The method can be used for films up to about 2000 Å. thick.

It has been shown¹⁷ that the above method, where reduction takes place in an open cell in contact with the atmosphere, is unreliable for very thin films (less than 100 Å.), and a closed-cell method has been developed which gives good agreement with the best optical methods in this range of thickness. The development of the electrolytic technique provides a satisfactory quantitative method by which the thickness of the separate parts of complex films can be measured. An X-ray

method has recently been used for the measurement of the parameters of oxide films on iron.¹⁸ This method could probably be used for thick films on copper (1000–10,000 Å.).

A method used by Pilling and Bedworth¹⁹ and others consists in measuring the change in resistance of a wire or thin film of metal due to the reduction of its current-carrying cross-section owing to oxidation. This technique was employed by Pilling and Bedworth for curves at 400° and 500° C., but does not seem to have been used extensively. Measurements of contact resistance provide yet another method by which film thicknesses may be estimated.²⁰ However, a precise knowledge of the composition of the film and of its electrical properties is necessary for accurate interpretation of the results.

One further method used in oxidation research,²¹ consists of measuring the decrease in pressure of the oxidizing atmosphere when the specimen is heated in a closed system. From this measurement the amount of oxygen absorbed by the specimen may be calculated.

The results described in the following sections have been obtained by one or more of the above methods, and in order to avoid lengthy descriptions, the following abbreviations have been used :

G = Gravimetric (whether continuous or interrupted).

ED = Electron diffraction.

O = Optical.

M = Metallographic (chiefly for subscale).

ER = Electrolytic reduction (open or closed cell).

DP = Decrease in pressure in closed system.

R = Increase in electrical resistance.

II.—THE OXIDATION OF PURE COPPER.

1. *Mechanism of Film Growth.*

In the oxidation of metals the rate of reaction in most environments is controlled by the rate at which metal or oxygen can penetrate the oxide layer. In general, as the oxide becomes thicker the rate of reaction becomes slower, provided that the film is continuous and therefore protective. The early gravimetric work of Pilling and Bedworth¹⁹ indicated that the type of oxidation depended upon the ratio of the volume of metal oxide to the volume of metal from which it forms, that is upon the ratio, $Wd : wD$, where W is the molecular weight of the oxide, w the weight of metal contained in W , D the density of the oxide, and d the density of the metal. If this ratio is less than unity the film will be discontinuous and will permit oxygen to reach the metal surface via the discontinuities. If the ratio is greater than

unity the initially formed thin film will be compact and continuous, but as it thickens discontinuities may appear as a result of thermal stresses or compression stress. The latter would be expected to be highest where the volume ratio greatly exceeds unity.

Metals for which the volume ratio is less than unity include barium, caesium, calcium, lithium, magnesium, potassium, sodium, strontium; for others of common practical interest, including copper, the ratios exceed unity, that for cuprous oxide on copper being about 1.7.

It may be shown that metals which form compact films (which grow by means of a diffusion process due to a concentration gradient) should oxidize according to the parabolic law, where the square of the weight, and hence the thickness, is proportional to the time, i.e. :

$$y^2 = Kt + A \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where y = thickness, t = time, and K and A are constants.

In the early work on copper this was found to be true, but departures from this relationship were found later. In the early stages of growth, especially at low oxygen pressures, the oxygen supply is not sufficient to cause oxidation of the metal atoms as fast as they diffuse to the surface, leading to a linear rate of growth :

$$y = Kt \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as was observed, e.g. by Wagner and Grünewald ²² using a gravimetric method at 1000° C., with an oxygen pressure of 1 mm. of mercury. The growth was linear up to a film thickness of 10⁻³ cm. after which it became parabolic.

Dighton and Miley ²³ have shown by the electrolytic-reduction method that for temperatures between 180° and 288° C. copper first oxidizes according to the parabolic law, and then as the time increases above 1-3 hr. the oxidation rate decreases, following the logarithmic relationship :

$$y = K \log a(t + 1/a) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

y , K , and t having the same meaning as in equation (1), and a being a constant.

Campbell and Thomas ²⁴ (*DP*) obtained an approximately cubic relationship of the type :

$$y^3 = Kt + c \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for the oxidation of oxygen-free copper between 100° and 256° C.

According to Cabrera and Mott ²⁵ the parabolic type of thickening can only be expected well outside the range of thickness over which a space charge is effective. This is about 10⁴ Å. in the case of copper. Anderson ²⁶ has also derived the cubic law for space-charge conditions,

when the mean free path is large compared with oxide thickness. If the mean free path is small a law of the type $y^4 = Kt$ would be expected. Cabrera²⁷ has explained theoretically the reasons for the cubic type of oxidation, and why a logarithmic law would be expected for film thicknesses obtained on copper below about 100° C. Such a relationship was found by Lustman and Mehl¹¹ for copper at temperatures between 88° and 155° C.

At low temperatures, in the vicinity of room temperature, Cabrera and Mott²⁵ suggest that the oxide film on copper should thicken logarithmically up to about 100 Å., and then stop. However, work carried out by Evans and Miley²⁸ at 80° C. shows that copper achieves a film thickness of approximately 100 Å. in about 5 hr., but that this is not the limiting thickness. At higher temperatures, Cabrera and Mott²⁵ recognize a type of thickening which is initially logarithmic but which later becomes parabolic.

At medium and high temperatures all evidence shows that copper ultimately follows the parabolic law. However, the rate-determining process may be either the outward diffusion of copper or the inward diffusion of oxygen. Bardeen, Brattain, and Shockley²⁹ and Castellan and Moore³⁰ have shown, by using radioactive tracers, that the diffusion of copper ions in cuprous oxide is the rate-determining factor in the oxidation of copper between 800° and 1000° C.

There is now considerable evidence for the view that in cuprous oxide films the metal atoms diffuse outwards by means of vacant sites in the oxide lattice. Wagner^{31,32} postulates that the diffusion of atoms through the oxide layer involves dissociation almost completely into ions and electrons. The cations and electrons move outwards and the anions inwards across the film. According to Hoar and Price's electrochemical interpretation³³ the growing film may be regarded as a current-producing cell with the metal/film and oxygen/film interfaces as the anode and cathode respectively and with the film serving both as electrolyte and external circuit, as it has both electronic and ionic conductivity. Thus it would seem that the resistance to oxidation is closely connected with the electrical resistance of the film.

According to Mott⁴ when Cu_2O is heated in oxygen its conductivity increases owing to stoichiometric excess of oxygen. It seems that the excess oxygen is not taken up interstitially, the oxygen atoms being too large to fit in the interstitial positions in the oxide lattice. The lattice accommodates excess oxygen through the absence from their normal lattice points of a few copper atoms. These vacant lattice points are mobile; i.e. an adjacent metal atom can move into them, and then another atom will move into the position which has been left vacant,

and so on. Thus the metal atoms move outwards during the oxidation of copper.

Dünwald and Wagner³⁴ (*G*) were able to show that Cu_2O films had an excess oxygen content of the order of 0.1%. However, Fröhlich³⁵ has demonstrated by the chemical analysis of thick films formed on copper at 900° and 1000° C. over a period of 5–21 days, that the films contain excess copper. Whereas the theoretical copper content of Cu_2O is 88.82%, Fröhlich obtained figures ranging from 88.82 to 89.31%. Rother and Bomke³⁶ have shown that in films on copper oxidized for long times at 1065° C., both the electrical conductivity and copper content vary markedly through the film as shown in Fig. 1. Lustman and Mehl¹¹ have shown a similar variability in thin films formed at low temperatures. It appears that the part of the oxide film near the metal surface is predominantly metallic and possesses metallic conductivity. If the scale is removed together with the above-mentioned layer and chemically analysed, a metal excess may result.

Dravnieks and McDonald³⁷ suggest that the consumption of metal due to outward diffusion should lead to voids on the oxide/metal interface. Either these will result in the collapse of the oxide film, producing new metal-to-oxide contact, or they must be filled with oxide due to inward diffusion of oxygen. Dravnieks postulates that the spaces are filled with columns of oxide which also act as conduits for the delivery of metal atoms to the bulk of the scale. Such a system suggests that oxidation proceeds both inwards and outwards from the original metal surface, and explains why the result of the complete oxidation of a copper wire is not a hollow "tube" of oxide but a comparatively solid oxide "wire". Dravnieks and McDonald³⁷ extend their theory to show how the existence of voids or cavity barriers leads to the slowing down of oxidation and hence to the logarithmic law, as also derived by Evans³⁸ (see below).

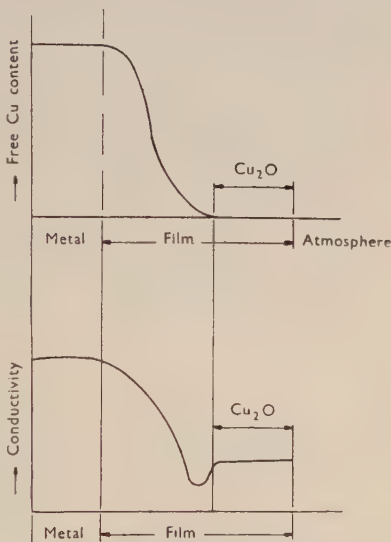


FIG. 1.—Change in Copper Content and Conductivity in Film on Copper (Rother and Bomke³⁶).

2. *The Effect of Internal Stresses.*

From the later work on copper and from work on other metals it is now clear that the volume ratio is only a rough guide to the oxidation characteristics of metals. Indeed, it has recently been shown by Gulbransen³⁹ that films on magnesium with a volume ratio 0.84 are

protective in certain circumstances. This is apparently due to the fact that these films, with a volume ratio less than unity, can stand considerable tensile stresses before they break down.

The existence of internal stresses in thin films formed on oxides with volume ratios greater than unity has been demonstrated by Evans.⁴⁰ The films were isolated by dissolving away the metal substrate, whereupon they assumed a wrinkled appearance. Films with a volume ratio exceeding unity, as they grow thicker, tend to break down in a number of ways owing to these compressive stresses. Evans³⁸ has recently put forward a theory showing how the manner of breakdown may lead to any one of the first three oxidation equations enumerated above. If adhesion between the metal and film is poor, and the strength of the film substance is high, a blister will be formed as in Fig. 2 (a). As the film thickens further, these blisters may lead to a porous film of type (b) or (c) in

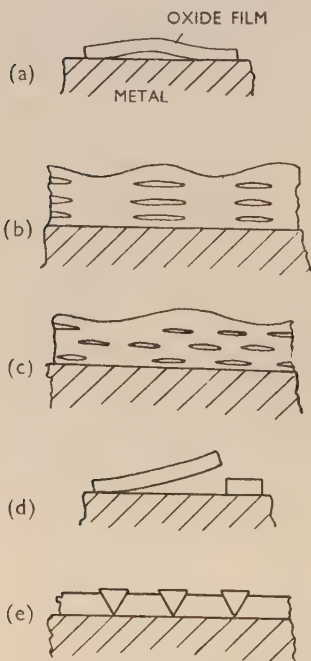


FIG. 2.—Forms of Film Breakdown
(Evans³⁸).

(a), (b), and (c) Blistering; (d) Flaking;
(e) Shear-Cracking.

Fig. 2. A less common form of breakdown is "flaking" ((d) in Fig. 2). This type is most likely to occur by the joining together of a large number of nearly continuous blisters. However, once flaking has started it is likely to spread rapidly. The third method of film breakdown is shown in (e) (Fig. 2). This is called "shear-cracking", and is most likely to occur where the adhesion between the metal and the film is good but the inherent strength of the film substance is relatively poor.

One possibility suggested by this theory is that the form of the specimen, i.e. bent wires or flat strip, may have a profound influence on the stresses in the films, and on the manner of breakdown and therefore on the oxidation law.

3. The Effect of Temperature.

When oxidation is a simple diffusion process, i.e. when the parabolic law is obeyed, the temperature dependence of the oxidation rate should be in agreement with the Arrhenius equation :

$$K = Ae^{-Q/RT} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where K is the "rate constant" ($\text{g.}^2 \text{ cm.}^{-4} \text{ hr.}^{-1}$), A is a constant

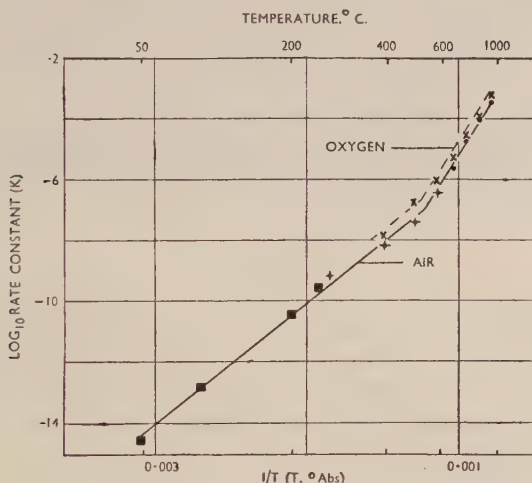


FIG. 3.—Oxidation Rate of Copper in Air and Oxygen.

- KEY
- × {Pilling and Bedworth¹⁹
Feitknecht⁴¹} in oxygen.
 - Pilling and Bedworth¹⁹ (in air).
 - + Hudson *et al.*⁴² (in air) (Cu + 0.47% As).
 - Vernon⁴³ (in air).

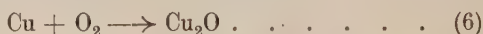
($\text{g.}^2 \text{ cm.}^{-4} \text{ hr.}^{-1}$), R is the gas constant, T the absolute temperature, and Q the activation energy (cal.).

When the logarithm of the oxidation rate is plotted against the reciprocal of the absolute temperature, a straight line should result. The rate constants obtained by Pilling and Bedworth¹⁹ and by Feitknecht⁴¹ for copper oxidized in oxygen (Fig. 3), when plotted in this way, appear to fall on two straight lines intersecting at about 580° C. The results of Hudson and his co-workers,⁴² and of Vernon⁴³ for copper

oxidized in air, if plotted in the same way, also form two straight lines which are parallel to those of Pilling and Bedworth.¹⁹

Scales formed on copper between 300° and 900° C. at normal pressure consist of two layers, CuO overlying Cu₂O. The relative thickness of the CuO layer tends to decrease as the oxidation temperature increases, since CuO dissociates at 1025° C. at 150 mm. pressure.

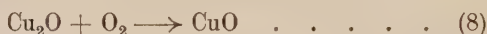
According to Valensi⁴⁴ the upper part of the curve (Fig. 3) results from the reaction :



This reaction can be made to proceed exclusively by the oxidation of copper between 900° and 1000° C. at pressures between 15 and 120 mm., respectively, i.e. below the dissociation pressure of CuO. For this reaction Valensi has obtained by calculation and confirmed by experiment the formula :

$$K = 957e^{-37,700/RT} \quad \dots \quad (7)$$

At low temperatures, corresponding to those giving the lower straight line in Fig. 3, Valensi gives the rate-determining reaction as :



for which he obtains the formula :

$$K = 0.054e^{-20,140/RT} \quad \dots \quad (9)$$

Formulae (7) and (9) define approximately the two straight lines shown in Fig. 3. These lines are, according to Valensi, the extreme tangents of a curve, and at intermediate temperatures the points in Fig. 3 represent a combination of reactions (6) and (8).

Table I shows the constant *A* and the activation energy *Q*, calculated

TABLE I.—*Comparison of Oxidation Constants Obtained by Various Investigators for Copper* ($K = Ae^{-Q/RT}$).

Type of Copper	Medium	Temperature Range, ° C.	Oxidation Constants		Reference
			<i>Q</i> , cal.	<i>A</i> , g. ² cm. ⁻⁴ hr. ⁻¹	
Tough-pitch .	Air	50– 250	19,300	0.056	Vernon ⁴³
“ .	“	700–1000	42,000	6300	Pilling and Bedworth ¹⁹
“ .	Oxygen	500– 900	29,400	50	“
“ .	“	750–1020	42,000	6300	Feitnecht ⁴¹
Oxygen-free .	Air	300– 550	20,140	0.054	Valensi ⁴⁴
“ .	“	550– 900	37,700	957	“
Tough-pitch .	“	715– 970	29,000	40	Krupkowski ⁴⁵
“ .	“	800–1030	41,000	6000	“
Arsenical .	“	300– 500	18,300	5×10^{-3}	Hudson, ⁴² <i>et al.</i>
(Grade not known)	“	800–1000	39,000	...	Castellan and Moore ³⁰

from the results obtained by different workers, for various temperature ranges. It is clear from the table that the activation energy corresponding to the high-temperature section of the oxidation range is of the order 29,000 to 42,000 cal., which corresponds fairly well with Valensi's figure of 37,700 cal. In the low-temperature range the data is rather meagre, but the activation energy obtained by Valensi of 20,140 cal. is well corroborated by Vernon⁴³ on pure copper, and Hudson *et al.*⁴² on arsenical copper (Table I).

4. Composition of Oxide Films on Pure Copper.

Cruzan and Miley¹⁵ studied the formation of cuprous and cupric oxide films on copper by the electrolytic-reduction method. Films of different thickness were formed by continuous heating at 240° C. in air for various times. It was found that all films less than 400 Å. thick consisted entirely of Cu₂O, while some of the films of an intermediate thickness (400–800 Å.) contained CuO, and all the films exceeding 800 Å. contained CuO. The thickness of the cupric oxide film never exceeded 150 Å. On the basis of their own results and those of Murison⁴⁶ (ED), and of Dunholter and Kersten⁴⁷ (ED), Cruzan and Miley put forward the following theory:

When diffusion through cuprous oxide films becomes sufficiently difficult cupric oxide is developed in the films, presumably from the oxidation of cuprous oxide. In this way the composition of the oxide film on copper is related to its total thickness. The thickness is a function of the temperature at which the film is produced, the period of time during which it is formed, the oxygen concentration in which it is developed, and any factor that might alter the permeability of the film, e.g. state of original surface, thermal stressing due to temperature cycle, &c. The presence of any cupric oxide nuclei due to the previous heat-treatment in the manufacture of the metal or otherwise, might cause a secondary reaction to start more readily and thus affect the relative proportions of cuprous and cupric oxide for such a material.

According to Cruzan and Miley prolonged heating produces thick CuO films which tend to exfoliate and can easily be separated from the underlying Cu₂O film. Murison⁴⁶ and later Miyake⁴⁸ (see Table II), both using electron-diffraction methods, have reported an oxide (designated CuO' in Table II) formed within the range 300°–500° C., which had a structure different from those of Cu₂O and CuO. The new pattern varied from that of normal CuO in that an additional diffraction was observed and the relative intensities of the rings were changed. Such differences suggest that the new oxide may in fact be

TABLE II.—*Oxide Films Obtained Using Two Methods of Heating (Miyake 48).*

Materials Examined	Heating Method †	Surface Products and Temperatures or Times of Oxidation After Which They Were Detected					Formation of Scale
		Cu ₂ O	CuO'	CuO	Other Oxide, if Observed		
Pure Copper (Cu 100%)	A	About 200° C.	300°-500° C.	(Experiments above 600° C. impossible)	...	Observed	
	B	Very short time	Short time (10-20 sec.)	Rather long time (few min.)	...	Observed	
7% Tin bronze	A and B	Almost the same as in the case of pure Cu					
Copper-7% manganese alloy							
Copper-7% nickel alloy							
Copper-7% magnesium alloy							
Aluminium bronzes : (97-90% Cu, 8-10% Al)	A	About 200° C.	300°-500° C.	600°-900° C.	...	Not observed	
	B	*	*	*	Al ₂ O ₃ after a few min.	Not observed	
(98% Cu, 2% Al)	A and B	Almost the same as in the case of pure Cu					
70 : 30 Brass	A	*	*	*	ZnO after a few min. at less than 900° C.	Not observed	
	B	Very short time (few sec.)	Short time (10-20 sec.)	Rather long time (few min.)	...	Not observed	
Beryllium bronzes (98-85% Cu, 2-15% Be)	A and B	*	*	*	BeO after a few min. at about 800° C.	Not observed	
Surface colour		Red (with an interference colour)	Black	Black	Al ₂ O ₃ retains almost original metallic lustre. ZnO yellowish white. BeO retains almost original metallic lustre		

* Indicates that the oxide was not detected.

† A : Heated in electric furnace (200°-950° C.). B : Heated in gas flame (slightly reducing).

an intermediate stage in the formation of the CuO , in which the atom sites are not occupied by copper and oxygen atoms in equal numbers.

Hickman ⁴⁹ (ED) shows that there is a change in composition with temperature, from pure CuO at 20° – 300° C., to a mixture of Cu_2O and CuO at 350° C., and 100% Cu_2O at temperatures above 450° C. The pressure used was equivalent to 1 mm., and there may have been some dissociation at the higher temperatures.

Valensi ⁴⁴ (G) has shown by theoretical treatment that ideally the composition of the oxide film on copper should vary with temperature from 98% CuO at 300° C. to 90% Cu_2O at 900° C., and gives experimental figures which agree well with the calculated ones as shown below :

Temperature, ° C.	Calculated	CuO, % Experimental
900	10.0	5.0
700	20.0	30.0
500	75.0	80.0
300	98.0	95.0

The discrepancy between these results and those of other workers is put down to the effect of the gas content of the copper, which Valensi minimized by vacuum-annealing for 12 hr. at 950° C. He ⁴⁴ found that the composition at 860° C. was constant irrespective of film thickness. His theory suggests that this should be true at all temperatures.

Palmer ⁵⁰ first detected the presence of CuO on copper at 165° C. on a highly activated (rough) surface.

5. Effect of Oxygen Concentration and Pressure.

The effect of oxygen concentration at 240° C. has been studied by Cruzan and Miley ¹⁵ (ED). They found that increasing the oxygen concentration increased the proportion of CuO in the film by a small amount, while decreasing the oxygen concentration by the admission of nitrogen into the furnace atmosphere, prohibited the formation of the CuO film entirely.

If the electrical theory of film formation is correct, increase in the oxygen pressure P should increase the electrical conductivity by increasing the number of ions and vacant spaces. Further, Mott has shown ⁴ that if complete dissociation into ions and electrons takes place, the electrical conductivity should vary as $P^{\frac{1}{2}}$, but if no dissociation takes place as $P^{\frac{1}{2}}$.

Dünwald and Wagner ³⁴ (G) heated copper at 800° , 900° , and 1000° C. in oxygen and measured the conductivity of the Cu_2O film formed. They found that it varied linearly as the seventh root of the pressure of oxygen. This indicates that dissociation was very nearly complete. The rate of oxidation was also proportional to the seventh root of the pressure.

Examination of Pilling and Bedworth's results ¹⁹ (G) shows a similar relationship for pressures in the range 800–0.3 mm. of mercury, at 800°C. However, below 0.3 mm.

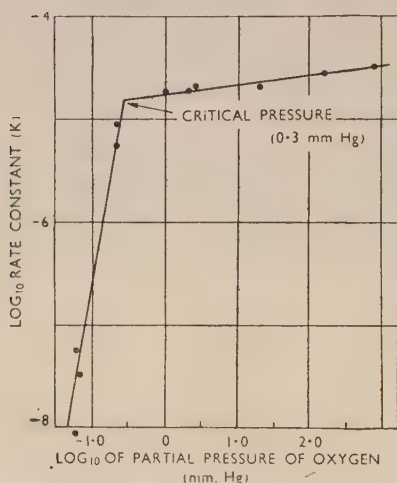


FIG. 4.—Effect of Oxygen Partial Pressure on Oxidation Rate of Copper at 800°C. (Pilling and Bedworth ¹⁹).

is adsorbed is the controlling factor, the film surface ceases to be saturated with adsorbed oxygen, and a rapid decrease in oxidation rate results. At low pressures the rate of gas flow past the heated specimen has a profound effect on the oxidation rate, as Pilling and Bedworth ¹⁹ (G) have shown (Table III).

TABLE III.—Effect of Rate of Gas Flow on Oxidation of Copper at 800°C. (Pilling and Bedworth ¹⁹).

Rate of Flow, c.c./min.	Oxidation Rate Constant K , $\text{g.}^2 \text{cm.}^{-4} \text{hr.}^{-1} \times 10^{-7}$
In oxygen mixture; oxygen partial pressure: 1.7 mm. Hg.	
14	0.046
95	0.77
110	10.00
245	36.0
550	70.0
In air; oxygen partial pressure: 155 mm. Hg.	
Open furnace	270
15	250
145	260

Palmer ⁵⁰ (*R*) found that below a pressure of 300 mm. on a highly activated surface, the oxidation-rate constant *K* was directly proportional to the partial pressure. Above this pressure the oxidation rate was substantially independent of pressure.

6. Orientation and Structure.

A number of investigators have determined the orientation of the oxide with respect to the metal surface. Preston and Bircumshaw ⁵² (*ED*) examined electrolytic copper oxidized in air at temperatures up to 400° C. It was found that the cuprous oxide film which was formed had a preferred orientation with the (111) plane parallel to the surface. No indication of possible preferred orientation of the underlying copper is given. The "activation" of the surface by repeated oxidation and reduction gave small crystals of Cu_2O with random orientation.

In contrast to Preston and Bircumshaw's results, Miyake ⁴⁸ (*ED*) reported that in many cases the crystals of cuprous oxide were orientated so that the (110) planes tended to become parallel to the surface. This agrees with Thompson, ⁵³ who found that the surface layer of his copper specimens was orientated with the (110) plane parallel to the surface and that the Cu_2O film formed had a similar orientation. Mehl, McCandless, and Rhines ⁵⁴ found that the orientation of the film was identical with that of the underlying copper lattice.

Lustman and Mehl ¹¹ made a comprehensive investigation of the oxidation of single crystals of copper at low temperatures. They found that at temperatures between 105° and 118° C. the rate of oxidation of different crystal faces varied. They thought that this was probably due to the observed difference in orientation between the metal crystal and the oxide crystal that formed on it. However, the relationship was very complex and varied with temperature.

Electron-diffraction studies by Phelps and his co-workers ⁵⁵ on the oxidation of copper in oxygen at 200° C. showed that the Cu_2O film was relatively coarsely crystalline. The size varied from a mean of 500 Å. at 5 min. to 750 Å. at 30 min. They were of the opinion that films containing small crystals were the most protective and that the coarse nature of the Cu_2O film was one reason for its non-protective character.

Smith ⁵⁶ (*ED*) showed that thin films formed on copper heated in air, and removed by dissolution in potassium sulphate, had no preferred orientation and consisted wholly of Cu_2O . Unheated films consisted of copper and Cu_2O , but the lattice of the copper was expanded 1.5%, which Smith thought might have been due to dissolved oxygen.

Bénard and Talbot ^{57, 58} (G) found that the oxidation rate of copper at 850°–900° C. increased with amount of cold work, owing to the increasing degree of preferred orientation. The rate of oxidation of single-crystal faces decreased in the following order :

$$\begin{array}{l} (210)-(221) \\ (211)-(110) \\ (111) \\ (100) \\ (123) \end{array}$$

According to Cabrera and Mott,²⁵ if the difference between the lattice parameters of the exposed plane of the metal and the oxide is less than 15%, the film will be pseudomorphous; if it is greater than this figure, the film will take up very nearly its own unstrained lattice parameter.

7. *Effect of Surface State.*

Films formed on smooth and mirror-like surfaces are less permeable than films formed on abraded surfaces containing corrugations, shattered metal, &c., resulting from abrasion treatment, according to Evans and Stockdale.⁵⁹ As the stage of growth at which CuO begins to form depends on the permeability of the film, it might be expected that CuO would form sooner on smooth surfaces than on rough ones. That this is so is shown by comparison between the electron-diffraction results obtained by Dunholter and Kersten⁴⁷ and by Miyake,⁴⁸ respectively. Dunholter and Kersten first detected CuO films at temperatures of from 120° to 180° C. (depending on oxidation time) on surfaces prepared by condensing copper on to glass. On emiered (0000) surfaces prepared by Miyake,⁴⁸ CuO was not detected below 300° C.

Lustman and Mehl,¹¹ using the optical method, found that for low temperatures (105°–155° C.) smooth surfaces oxidized more slowly than rough surfaces. Bénard ⁵⁸ (G) found that the rate of oxidation of copper at high temperatures fell as the surface roughness was decreased. This presumably was due to a decrease in the true surface area. Gulbransen ⁶⁰ and Valensi ⁴⁴ have pointed out that the effect of a rough surface will be to show initially an apparent reduction in oxidation rate, since the true surface area will lessen as oxidation smooths out inequalities.

8. *Effect of Other Atmospheres.*

Dyess and Miley ⁶¹ (ER) determined the thickness of films on copper which were mixtures of cupric oxide, cuprous oxide, and cuprous sulphide. When oxide-coated copper was exposed to moist hydrogen

sulphide in air at room temperature, copper sulphide was formed, owing partly to combination of some sulphur with copper from the metal and partly to the replacement of some of the oxygen in the oxides by sulphur. No evidence was obtained of the replacement of sulphur by oxygen at 220°–270° C. when sulphide films were heated in air in an electric furnace. Thin oxide films containing pores, and thick ones with cracks, give poor protection against H_2S . It was observed that sulphide films gave more protection against attack by moist H_2S than oxide films of similar thickness. Dyess and Miley suggest that the specific conductivity of the sulphide may be less than that of the oxide.

To some extent this work contradicts the results of Vernon,⁶² who found that impure oxide films containing sulphide exposed to air at room temperature had lower oxidation-resistance than pure oxide films. Pure sulphide films not only caused a greater attack on the underlying metal than pure oxide or oxysulphide when exposed to ordinary air (containing some sulphur), but also selectively absorbed sulphur from the atmosphere. On the other hand, sulphur is virtually unable to penetrate pure oxide films.

The effect of atmospheres containing steam and water vapour has been studied by Preston and Bircumshaw⁵² (*ED*) and by Hallowes and Voce⁶³ (*G*). Treatment for 1 hr. in steam at 100° C. gave Cu_2O , and a second phase which was thought to be CuO .⁵² The introduction of 10% water vapour made little difference to the rate of oxidation in air at 400° C.⁶³ At 400° C. the effect of additions of SO_2 and Cl to the atmosphere⁶³ was to increase the oxidation rate, particularly in the presence of moisture.

Vernon⁶⁴ found that up to 10% of SO_2 in dry air had no effect on the oxidation rate of copper at room temperature. However, there was a big increase in the oxidation rate when the relative humidity exceeded about 63%. The effect of additions of CO_2 to atmospheres containing SO_2 and water vapour was negligible. The effect of 0.01% HCl , with and without SO_2 and water vapour, was to produce a marked increase in oxidation rate.

There is considerable evidence that pure steam and pure water vapour have little effect on the oxidation of copper up to 800° C. at atmospheric pressure.^{19, 84} However, in the case of steam the impurities present in the water from which it is formed may exert a considerable effect, as has been shown by Hallowes and Voce⁶⁵ for an aluminium bronze. In the case of reducing atmospheres, the presence of CO_2 , H_2O , and H_2S may markedly affect the scaling properties.

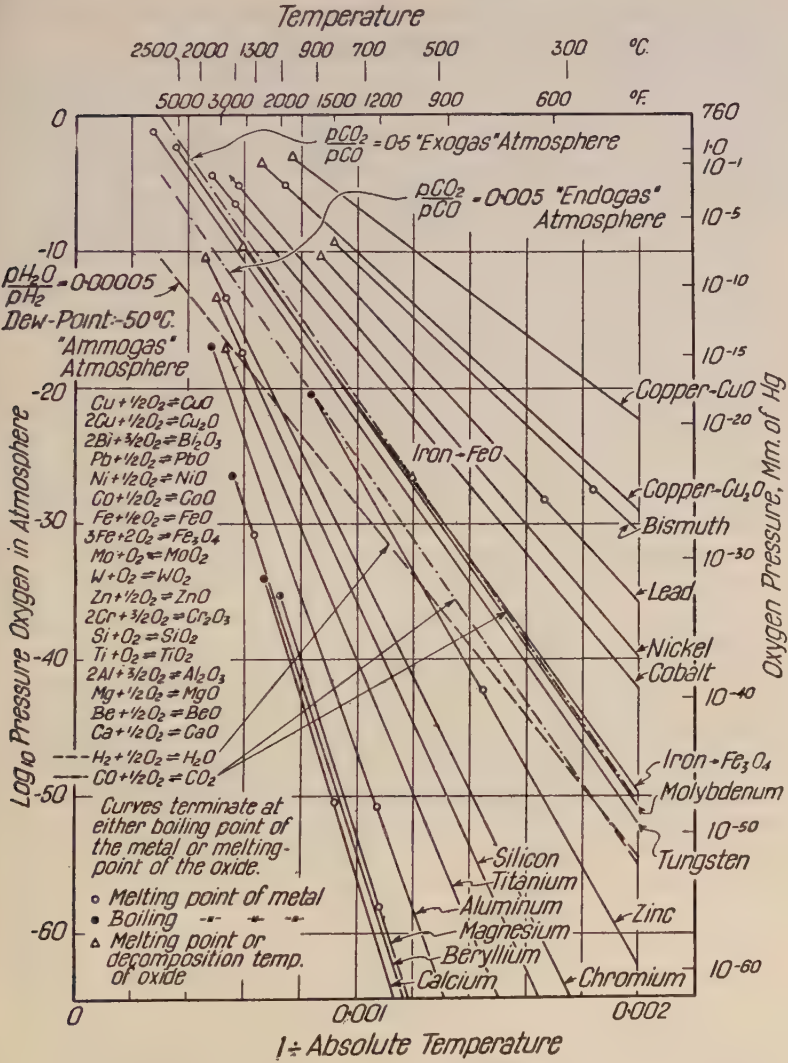
III.—EFFECT OF IMPURITIES AND ALLOYING ELEMENTS ON OXIDE FILMS ON COPPER.

1. *Surface Scale.*

Metal oxides differ considerably with regard to their stability. Whereas silver oxide is relatively unstable and can be decomposed when heated to a moderate temperature, oxides of aluminium, magnesium, and beryllium are extremely stable, and can be reduced only with great difficulty. The stability of an oxide is measured by its standard free energy of formation ($-G^\circ$), the more refractory oxides (aluminium, magnesium, beryllium) having high free energies, and the less refractory oxides, of silver, copper, &c., having low free energies. A considerable amount of information on this subject has been collected recently by Ellingham,⁶⁶ and by Richardson and Jeffes.⁶⁷ To the industrial metallurgist and others interested in oxidation problems the dissociation pressure of an oxide is more valuable than the standard free energy of formation. The dissociation pressures of many oxides have been calculated by Lustman,² and are given in Fig. 5.

In regard to oxidation, copper alloys form two main groups: (1) alloys with noble metals, which form substantially pure Cu_2O scales, and (2) alloys with baser metals, where the alloying element appears as an oxide in the scale, often in greater concentration than in the alloy itself and sometimes to the exclusion of Cu_2O . The oxides of the noble metals have higher dissociation pressures than Cu_2O , and hence their oxides are not present in films on copper-base alloys. However, the majority of copper-base alloys fall into the second class. Under mildly oxidizing conditions, i.e. with low partial pressures of oxygen, it is possible for the oxide of the baser metal, e.g. alloying elements such as aluminium, beryllium, or silicon, to form exclusively and in preference to Cu_2O . During the early stages of the oxidation of a binary alloy of copper and a baser metal, both oxides will form. Whether or not the oxidation rate of the alloy is less than that of copper will depend on the concentration of the alloying element and the relative diffusion velocities of metal atoms (or ions) in the oxide layers.

Contributions on the theory of the oxidation of binary alloys have recently been made by Smirnov and Orlov^{68, 69} Smirnov⁶⁸ concludes that the formation of a protective oxide film may be expected when the diffusion velocity of one of the metals becomes small compared with the other as the film thickens. If the diffusion constants of the two metals in the nearly pure oxide of the alloying elements are sufficiently small, the growth of the film will be greatly retarded, and it will have good oxidation-resistant properties. Orlov and Smirnov⁶⁹ extend this



[Courtesy of American Society for Metals.]

FIG. 5.—Curves of Dissociation Pressures of Metal Oxides Formed at Various Temperatures on Several Common Metals (Lustman²).

theory to explain the loss of oxidation-resistance which some alloys undergo as the temperature rises, and how this may be offset by increasing the concentration of the alloying element. Some actual

examples are taken from the experimental results of other workers to show how these agree with theoretical predictions.

On the experimental side, some investigators have examined the effects of the addition of a large number of elements on the oxidation-resistance of copper. Many others, however, have examined the effect of one element over a restricted, or sometimes a considerable, range of compositions. It is proposed therefore first to discuss the experimental results of those workers who have dealt with a wide range of different binary and ternary alloys and compared their oxidation-resistances. The results of the other workers in the oxidation field will be collectively discussed under the various alloys investigated. The range of information available is summarized in Table IV.

Miyake⁴⁸ investigated a range of copper-base alloys by electron diffraction. Two methods of heating were used, one described as method *A* in which the specimens were brought to temperatures between 200° and 950° C. over a period of 10 min. in free air, and the other (*B*), where the specimens were placed directly in a slightly oxidizing flame and brought up to 800° C. in a very short time.

The results of Miyake's experiments are summarized in Table II. The differences in behaviour of aluminium bronze under the conditions of methods *A* and *B* are ascribed to the insufficiency of oxygen in the gas flame, which probably prevented the formation of CuO. Miyake deduced that the affinity of aluminium for oxygen led to its selective oxidation. It is probable that with the *A* method of heating, an Al₂O₃ scale is formed beneath CuO and Cu₂O. On aluminium bronzes containing more than 3% aluminium, γ -alumina formed underneath the superficial Cu₂O film after prolonged heating in a gas flame. There was no change in surface colour. The surface film on 70:30 brass heated in air corresponded to pure ZnO and was yellowish-white in colour. BeO was formed on the surface of beryllium bronze at high temperatures with both heating methods.

Fröhlich³⁵ (*G*) investigated the oxidation in air of a wide range of copper-base alloys at 800° C. with times up to 24 hr. A summary of his results is given in Table V. Of the alloys investigated the most resistant were those containing aluminium, beryllium, or magnesium. The next most resistant were alloys containing large amounts of tin or zinc. The effect of large additions of arsenic, cerium, and chromium was to increase the oxidation rate.

Fröhlich also made a study of the oxidation of nickel silver (nickel 18, zinc 21%), where he found that preferential oxidation of the zinc had occurred, as shown in Table VI.

Campbell and Thomas²⁴ (*DP*) determined the oxidation rates in

TABLE IV.—*Summary of Information Available on Oxidation of Copper-Base Alloys.*

Alloying Element(s)	Composition Range, %	Temperature Range, °C.	Atmosphere	Method *	Ref.	Notes
Ag	1.0 1.0 4.0 0-100 0-100	400 600-1000 700 600-750	Various Air, Cu ₂ O + Cu Air Air and oxygen	G M G G	63 73 35 70	Subscale
Ag-Au Ag-Pd	Ag 0-62, Au 10-59 Ag 40-94, Pd 0-40	750	Oxygen	G	71	
Al	0.01-0.91 0.03-0.72 1.0-3.0 2.0-12.0 2.0-10.0 0-10	600-1000 600-1000 800 400 200-950 700	} Air, Cu ₂ O + Cu Air Various Air and gas Air	M M G G ED G	73 74 35 63 48 75	Subscale
Al-As Al-Be Al-Cr Al-Fe	Al 8.0, 10.0, As 0-1.0 Al 0.049, Be 0.003 Al 8.0, 10.0, Cr 0-1.0 Al 10.0, Fe 2.8	700 600-1000 700 400		G M G G	75 74, 73 75 63	
Al-Fe-Ni	Al 8, 10, Fe 0-4.0 Al 10.0, Fe 5, Ni 5	700 400	Air Steam + SO ₂ + chlorine	G G	75 65	
Al-Mn	Al 8, 10, Mn 0-4 Al 7.0, Mn 4.0	700 180-400	Air Oxygen	G ED	75 52	
Al-Ni Al-Si Al-Ti	Al 8, 10, Ni 0-4.0 Al 4, 6, Si 0-5.0 Al 8, 10, Ti 0-4.0	700	Air	G	75	
As	0.46 0-1.0 0.03-0.12 9.5 0.47	400 700 600-1000 800 300-600	Various Air Air, Cu ₂ O + Cu Air Air, chlorine, &c.	G G M G G	63 75 73 35 42	Subscale
Au Au-Pd	90, 95 0-100 Au 33.3, Pd 0-61.7	300-950 750 750	Air Oxygen "	G G G	72 71 71	
B	0.005	600-1000	Air, Cu ₂ O + Cu	M	74, 73	
Ba	0.10	600-1000	Air, Cu ₂ O + Cu	M	74, 73	
Be	0.018-0.10 0.005-0.10 0.38-2.4 2.0-15.0 0.49-9.96 1.5-3.0	600-1000 600-1000 800 200-950 610-910 400	Air, Cu ₂ O + Cu " Air Air and gas Air "	M M G ED G G	73 74 35 48 76 77	Subscale
Be-Ni	Be 2.0-2.5, Ni 0.25 max.	100-300	Oxygen	DP	24	
Bi	0.03	600-1000	Air, Cu ₂ O + Cu	M	73	Subscale
Ca	trace 1.0 0.01	600-1000 800 600-1000	Air, Cu ₂ O + Cu Air Air, Cu ₂ O + Cu	M G M	73 35 74	Subscale
Cb	0.04	600-1000	Air, Cu ₂ O + Cu	M	74, 73	
Cd	0.25-0.28 1.0	600-1000 400	Air, Cu ₂ O + Cu Various	M G	73 63	Subscale
Ce	0.01 5.0	600-1000 800	Air, Cu ₂ O + Cu Air	M G	74, 73 35	

* G = gravimetric. M = metallographic. ED = electron diffraction.
DP = decrease in pressure in closed system.

TABLE IV.—(continued).

Alloying Element(s)	Composition Range, %	Temperature Range, °C.	Atmosphere	Method *	Ref.	Notes
Co	0.14	600–1000	Air, Cu ₂ O + Cu	M	74, 73	
Co-Si	8.0 Co 2.7, Si 0.4	800 800–1050	Air "	G G	35 79	
Cr	0.08–0.10 0.08 2.0	600–1000 600–1000 800	Air, Cu ₂ O + Cu " Air	M M G	73 74 35	Subscale
Fe	0.1 0.037–2.65 7.75	600–1000 600–1000 800	Air, Cu ₂ O + Cu " Air	M M G	73 74 35	Subscale
Fe-Ni-Co	Fe 18, Ni 18, Co 10	100–300	Oxygen	DP	24	
Ga	0.03	600–1000	Air, Cu ₂ O + Cu	M	74, 73	
Ge	0.2	600–1000	Air, Cu ₂ O + Cu	M	73	Subscale
In	0.25	600–1000	Air, Cu ₂ O + Cu	M	73	Subscale
Li	0.02 0.67	600–1000 800	Air, Cu ₂ O + Cu Air	M G	74 35	
Mg	0.7–2.76 0.10 7.0	800 600–1000 200–950	Air Air, Cu ₂ O + Cu Air and gas	G M ED	35 74, 73 48	
Mn	0.03–1.55 4.0 5.0 7.0 0–20	600–1000 400 800 200–950 700	Air, Cu ₂ O + Cu Various Air Air and gas Air	M G G ED G	74, 73 63 35 48 75	
Na	0.1	600–1000	Air, Cu ₂ O + Cu	M	73	Subscale
Ni	1.0, 20 3.0 7.0–70 0.1–5.0 7.0 0–70 44.0 0–100 0–100	800 400 300–900 600–1000 200–950 700 20–400 750–1000 300–800	Air Various Air and gas Air, Cu ₂ O + Cu Air and gas Air " Oxygen " (1 mm.)	G G ED M ED G ED	35 63 80 74, 73 48 75 78 81 82	
Ni-B	Ni 5.2, B 0.38 Ni 7.0, B 0.5	800	Air	G	35	
Ni-Be-Si	Ni 45, Be 1.0, Si 1.0–2.0	600–1000	"	W	83	
P	0.05, 0.54 0.03–0.24 0.03–2.05 0.25	800 600–800 600–800 400	Air Air, Cu ₂ O + Cu " Various	G M M G	35 74 73 63	Subscale
Pb	0.03	600–1000	Air, Cu ₂ O + Cu	M	74, 73	
Pd	0.20 0–100	600–1000 750	Air, Cu ₂ O + Cu Oxygen	M G	73 71	Subscale
Pt	0.10 90, 95	600–1000 300–1550	Air, Cu ₂ O + Cu Air	M G	73 72	Subscale
S	0.02	600–1000	Air, Cu ₂ O + Cu	M	73	Subscale
Sb	2.4	800	Air	G	35	
Se	0.1	600–1000	Air, Cu ₂ O + Cu	M	73	Subscale

* G = gravimetric. M = metallographic. ED = electron diffraction.
W = electric heating of wire (life test). DP = decrease in pressure in closed system.

TABLE IV (continued).

Alloying Element(s)	Composition Range, %	Temperature Range, °C.	Atmosphere	Method *	Ref.	Notes
Si	0.045-1.9 0.5-3.0 1.0 0-8.0	600-1000 800 400 700, 800	Air, Cu ₂ O + Cu Air Various Air	M G G G	74, 73 35 63 75	
Si-Fe	Si 0.9-4.5, Fe 0.06-0.28	725, 827	Air + oxygen	G	84	
Si-Mn	Si 3.0, Mn 1.0	400	Various	G	63	
Si-Mn-Fe	Si 3.0, Mn 1.0, Fe 0.09	100-300	Oxygen	DP	24	
Si-Ni	Si 0.5, Ni 0.75	400	Various	G	63	
Sn	0.31 2.0 2.8-20.0 7.0 0-16.0	600-1000 400 800 200-950 700	Air, Cu ₂ O + Cu Various Air Air and gas Air	M G G ED G	74, 73 63 35 48 75	
Sn-Al	Sn 5.4, Al 0.06	600-1000	Air, Cu ₂ O + Cu	M	74, 73	
Sn-Be	Sn 0.3-5.0, Be 0.006-0.02	600-1000	"	M	73	Subscale
Sn-P	Sn 6.1, P 0.54	800	Air	G	35	
	Sn 1.9-5.0, P 0.007-0.11	400	Various	G	63	
	Sn 7.5-8.5, P 0.03-0.2	100-300	Oxygen	DP	24	
Sn-Si	Sn 5.02, Si 0.085	600-1000	Air, Cu ₂ O + Cu	M	73	Subscale
Sr	0.10	600-1000	Air, Cu ₂ O + Cu	M	73	Subscale
Ta	0.05	600-1000	Air, Cu ₂ O + Cu	M	74, 73	
Te	0.10	600-1000	Air, Cu ₂ O + Cu	M	73	Subscale
Ti	0.05 4.0 20	600-1000 800 300-800	Air, Cu ₂ O + Cu Air Oxygen (1 mm.)	M G ED	74, 73 35 49, 85	
Tl	0.03-0.49	600-1000	Air, Cu ₂ O + Cu	M	73	Subscale
V	0.09	600-1000	Air, Cu ₂ O + Cu	M	73, 74	
W	0.10	600-1000	Air, Cu ₂ O + Cu	M	73	
Zn	0.16-0.21 3.22 5.0-40 0.40 0-100 30 30 0-35 30, 38 40	600-1000 400 800 580-880 300-900 200-950 100-400 700 20-300 200-425	Air, Cu ₂ O + Cu Various Air Air + oxygen Air, Cu ₂ O + Cu Air and gas Air " "	M G G G M ED ED G	73, 74 63 35 84, 86 87 48 52 75 78	
	26.5-35.5	100-300	Oxygen	DP	24	
Zn-Al	Zn 26-29, Al 2	100-300	"	DP	24	
	Zn 30, Al 0.2-0	775	"	G	84, 88	
	Zn 22, Al 2.0	100-400	Air	ED	52	
	Zn 9.29, Al 0.13	600-1000	Air, Cu ₂ O + Cu	M	73, 74	
Zn-Be	Zn 9.52, Be 0.03	600-1000	"	M	73	Subscale
Zn-Ni	Zn 21, Ni 18	800-950	Air	G	35	
	Zn 18, Ni 20	20-300	"	ED	78	
	Zn 25-29, Ni 16-20	100-300	Oxygen	DP	24	
Zn-Si	Zn 9.81, Si 0.085	600-1000	Air, Cu ₂ O + Cu	M	73	
Zr	0.16 60	600-1000 300-800	Air, Cu ₂ O + Cu Oxygen (1 mm.)	M ED	73, 74 49, 85	

* G = gravimetric.

M = metallographic.

ED = electron diffraction.

DP = decrease in pressure in closed system.

TABLE V.—*Effect of Alloying Elements on Oxidation-Resistance of Copper (Fröhlich ³⁵).*

Group	Alloying Element and Content, %			Oxidation-Resistance
1	Be (2.4)	Al (2.5, 3.0)	Mg (2.76)	Very high
2	Zn (20-40)	Sn (8.6, 20.0)	Be (1.0)	High
3	Ni + B (5.2-7.0 Ni, 0.38-0.5 B)			Fair
4	Ag (4.0) Li (0.67) Ca (1.0) Mn (5.0) Ni (1.0, 20.0)	Co (8.0) P (0.05, 0.54) Sb (2.4) Fe (7.75) Ti (4.0)	Mg (0.7) Sn (2.8) Zn (5.0) Be (0.38) Si (0.5-1.8)	About the same as copper
5	As (9.5)	Cr (2.0)	Ce (5.0)	Inferior to copper

TABLE VI.—*Change in Composition of Nickel Silver Due to Oxidation at 950° C. (Fröhlich ³⁵).*

Element	Time, hr.		
	0	15	36
Cu, % . . .	60.7	62.6	67.0
Ni, % . . .	17.7	18.5	18.7
Zn, % . . .	21.6	18.9	14.0

the temperature range 100°-300° C. of a number of binary and ternary copper-base alloys. These included 2% beryllium copper, Everdur, phosphor bronze (8% tin), 70 : 30 and 67 : 33 brasses, nickel silver, aluminium brass, and a copper-iron-nickel-cobalt alloy.

The oxidation of the phosphor bronze, copper-nickel-iron-cobalt alloy, and 70 : 30 brass was of the same type as that of copper, with somewhat lower oxidation rates. The oxidation rate of the other materials, however, decreased to a very low value, the oxygen absorbed in 1 hr. at 200° C., being of the order of $\frac{1}{20}$ th that of copper.

Nishimura ⁷⁵ (G) determined the oxidation properties of a number of α -solid solutions of copper at 700° C. in air. He found that the aluminium bronzes were the most resistant, 8% aluminium being required for maximum resistance. The next best were nickel and tin alloys, up to 40% and 16% (the maximum investigated), respectively, being required for maximum resistance. The optimum silicon content was 4%; increasing the silicon content to 8% resulted in a decreasing oxidation-resistance. The effect of zinc was determined up to 35%, about 20% being sufficient to give maximum resistance. Additions of

up to 20% manganese caused a continuous increase in oxidation-resistance. The effect of up to 1% arsenic was negligible.

Under conditions of intermittent oxidation, which are more representative of practical oxidation conditions, the least resistant materials tend to produce exfoliating scales, while the more resistant materials form adherent scales. Hallowes and Voce⁶³ (G) investigated five varieties of commercial copper and eighteen copper-base alloys for resistance to intermittent oxidation at 400° C. in five atmospheres. The alloys studied may be divided into three groups :

(a) Alloys containing 2–12% aluminium (one with 10% aluminium + 2·8% iron).

(b) Binary alloys containing small amounts of silver, cadmium, chromium, manganese, nickel, phosphorus, silicon, tin, zinc.

(c) Three industrial alloys, containing respectively : (1) 3% silicon + 1% manganese, (2) 0·5% silicon + 0·75% nickel, and (3) 5% tin + 0·1% phosphorus.

The atmospheres other than dry air included : air + 10% H₂O, dry air + 0·1–5% SO₂, and moist air + 0·1% HCl.

Their conclusions were that with the exception of silver all elements effected an improvement to a greater or lesser extent in the oxidation-resistance of copper to dry air, silicon and aluminium being the most effective. The introduction of 10% of water vapour into the atmosphere made little difference except to tin bronzes, the oxidation of which was approximately doubled. 0·1% SO₂ in dry air generally increased attack, and moist air + HCl was exceedingly detrimental. The most resistant materials were the high-aluminium bronzes, with or without iron, and the 3% silicon + 1% manganese alloy.

Copper-Zinc.

Dunn⁸⁴ (G) observed the oxidation of copper-zinc alloys, containing from 60 to 100% copper, in air at temperatures from 580° to 880° C. In alloys containing from 28 to 40% zinc the scale consisted almost entirely of ZnO, while in alloys containing 0–12% zinc the scale contained copper in the same proportions as in the alloy. In these two groups the rate of oxidation at constant temperature conformed with the parabolic law, but for the intermediate range of alloys (12–28% zinc) the oxidation rate was much less than that corresponding to the parabolic law, and the departure was ascribed to an increase in the grain-size of the film. With one exception the logarithm of oxidation rate was proportional to the reciprocal of the absolute temperature. The addition of water vapour, CO₂, or dry SO₂ to dry oxygen was found

to have no accelerating effect on the rate of oxidation, although wet SO_2 produced a considerable increase and HCl was most damaging.

Rhines and Nelson ⁸⁷ (*M*) have investigated the microstructure of copper-zinc alloys (0–100%) after heating between 300° and 900° C. Two methods of heating were used : heating with free access to air in an electric muffle, and heating in an iron vessel packed with a mixture of Cu_2O and copper metal powder or foil.

Cu_2O was present in the external scale on alloys containing up to 20% zinc heated in air, over the whole temperature range. At low zinc concentrations the Cu_2O is the matrix of the scale and contains embedded particles of ZnO in greatest concentration near the metal surface. As the zinc content of the alloy increases, the ZnO adjoining the metal surface becomes a continuous film, and with even higher zinc contents Cu_2O occurs only as occasional particles in the ZnO film. No Cu_2O forms on samples heated in the Cu_2O – Cu mixture, the scale consisting entirely of ZnO .

Continuous films of ZnO are formed on alloys containing more than 20% zinc oxidized in air. This film is relatively thin and tends to spall on cooling. No continuous film of ZnO is found on the surfaces of samples heated in the Cu – Cu_2O pack, but isolated patches do appear on or just below the surface.

Copper-Zinc-Aluminium.

The effects of additions of aluminium to 70 : 30 brass were investigated by Dunn ⁸⁴ (*G*) and 1.9% aluminium was found to reduce the oxygen absorbed in 3 hr. at 775° C. in oxygen from 1.0 to less than 0.02 mg./cm.². Preston and Bircumshaw ⁵² (*ED*) also investigated the behaviour of 70 : 30 brass with up to 2% aluminium at 100°, 183°, and 400° C. in air. It was found that the effect of aluminium was to inhibit formation of a Cu_2O film on the surface at 100° C. Cu_2O was present at 183° C., and at 400° C. ZnO was also present.

Copper-Silver.

Leroux and Raub ⁷⁰ (*G*) studied the oxidation of the whole range of copper-silver alloys, at 600° and 750° C. in air and oxygen.

More recent work by Raub and Engel ⁷¹ (*G*) was carried out at 750° C. in oxygen for times up to 70 hr. Oxidation of alloys containing from 10 to 80% silver was approximately parabolic. In the case of alloys containing 90 and 94% silver, the rate was more rapid at first but tended to negative values later. Minima occurred in each of the curves of oxygen absorbed against silver content of the alloy, at about 70 and 100% silver. The maximum oxidation rates occurred at 100% copper and 85% silver.

Raub and Engel ⁷¹ found that alloys rich in copper (e.g. 50% copper) form a homogeneous scale of Cu_2O overlying a subscale of Cu_2O and silver. In the case of alloys containing more than 72% silver oxidation proceeds solely by the formation of a subscale of ever-increasing thickness. At reduced oxygen pressures, i.e. in air, there is a tendency for CuO to form instead of Cu_2O .

Copper-Gold.

Raub and Engel ⁷¹ also investigated the oxidation of copper-gold alloys from 0 to 95% gold, at 750° C. The amount of oxygen absorbed per gramme of copper decreases slightly with increase of gold content up to 58%; after that there is a rapid decrease to zero at 100% gold. The 5% copper alloy has a thin film of CuO after 30 hr. at 750° C. due to the low diffusion rate of oxygen in gold. Increasing copper content results in the formation of an outer layer of Cu_2O and an inner scale layer of Cu_2O and gold.

Kubaschewski ⁷² (G) showed that copper-gold alloys containing 5–10% copper follow the parabolic law. He points out that the volume ratio of Cu_2O to that of the alloy is much smaller than that of Cu_2O to copper (= 1.65), and on this basis explains the good adherence of Cu_2O scales on gold-copper and platinum-copper alloys. Kubaschewski gives the following constants for the Arrhenius equation :

Alloy	Temperature Range, ° C.	A ($\text{g.}^2 \text{ cm.}^{-4} \text{ hr.}^{-1}$)	Q (cal.)
Gold-5% copper	500–900	675	11,200
Gold-10% copper	400–870	11×10^4	11,500

Copper-Platinum.

According to Kubaschewski ⁷² (G) platinum alloys containing 5% and 10% copper also follow the parabolic law. The activation energy for the 10% copper alloys was 11,800 cal. and A was 42 ($\text{g.}^2 \text{ cm.}^{-4} \text{ hr.}^{-1}$). In the region of 900° C. the oxide dissociated, until at about 1200° C. there was a loss in weight, probably due to volatilization of copper. However, there seems to be some evidence for the existence of a gaseous platinum oxide at 1100°–1400° C.

Copper-Palladium.

Raub and Engel ⁷¹ (G) investigated a range of copper-palladium alloys containing from 0 to 95% palladium. They found a minimum in the oxygen absorbed per gramme of copper at 30–40% copper. The curves had much the same parabolic form as those of the gold-copper alloys, but the oxidation rate of the 95% palladium alloy was only half that of the 95% gold alloy.

Cu-Au-Ag, Cu-Au-Pd, and Cu-Pd-Ag.

Raub and Engel⁷¹ also examined ternary alloys containing 10–58.5% gold, 0–85% silver, remainder copper; 33.3% gold, 0–61.7% palladium, remainder copper; and 6–20% copper, 0–54% palladium, 40–94% silver.

Copper-Nickel.

Dunn⁸⁴ (G) states that the addition of up to 1% nickel has no effect upon the oxidation rate of pure copper.

Miyake⁸⁰ carried out electron-diffraction experiments on copper-nickel alloys containing 7% nickel, 40% nickel, and 70% nickel + 1.4% iron + 1.0% manganese (Monel). He found that the outer layers of the film formed in air at 300°–900° C. on alloys containing 7% nickel consisted solely of copper oxides. When these oxides were removed (the method is not stated) from an alloy containing 7% nickel, a brown film appeared which had a lattice constant corresponding to NiO.

Hickman and Gulbransen⁸² (ED) examined a range of copper-nickel alloys containing 12–90% nickel, in the temperature range 300°–800° C. NiO was observed in the outer layers of the film at increasing temperatures varying from 500° to 800° C., as the nickel content of the alloy was reduced from 90 to 12%. The authors thought that the reason for the reduction of the oxidation rate with increasing amounts of nickel was the effect of nickel on the diffusion rate of copper through the film. It also appears that copper ions form and diffuse faster through the film than nickel at low temperatures, but that the position is reversed at higher temperatures.

Hessenbruch⁸³ reports that additions of 1% beryllium, 2% silicon, and 1% beryllium + 1% silicon increase the permissible working temperature of Constantan (45% nickel–55% copper) from 600° to 800° C. With the 1% beryllium + 1% silicon addition, the life of a 0.016 in. dia. wire was extended from 36 to 314 hr., using a heating cycle consisting of 2 min. on and 2 min. off (temperature not stated).

Copper-Titanium and Copper-Zirconium.

Hickman and Gulbransen⁸⁵ (ED) found that on 80 : 20 and 72 : 28 copper-titanium alloys, TiO₂ only appeared on the surface of the oxide film at temperatures above 500° C. In the case of a 40 : 60 copper-zirconium alloy, they found that zirconia was completely absent from the surface up to the maximum temperature investigated of 700° C.

Copper-Silicon.

Dunn⁸⁴ (G) investigated a number of copper-silicon alloys containing from 0.9 to 4.6% silicon and from 0.06 to 0.28% iron, at 725° and

827° C. 4.58% Silicon reduced the rate of oxidation at 725° C. to one-quarter of that of pure copper. Smaller amounts had a correspondingly smaller effect. A tightly adherent scale was produced which, when removed in HCl, left a dull transparent film which was thought to be silica. The ratio of copper : silicon in the scale and film together was substantially the same as in the metal.

While at 827° C. an alloy containing 0.9% silicon oxidizes at approximately the same rate as copper, alloys containing 3.25 and 4.58% silicon oxidize initially at about one-third the rate for copper. After a short time, however, the rate increases to approximately that of copper. The scale from alloys oxidized at this temperature was found to contain practically no silicon, and it is therefore not surprising that the final oxidation rate approximated to that of copper.

The explanation put forward by Dunn⁸⁴ to account for this result is that the initial film formed on the alloys of high silica content contains some silica in solid solution which renders the film less permeable, but that at a later stage the silica is reduced by copper, assuming that the solubility of silica in Cu_2O is appreciable and that of silicon negligible so that the reaction $\text{SiO}_2 + 4\text{Cu} \rightleftharpoons 2\text{Cu}_2\text{O} + \text{Si}$, which normally proceeds to the left, is reversed and proceeds to the right, the silicon freed entering into solid solution in the metal.

Nishimura⁷⁵ (G) studied the oxidation in air at 700° and 800° C. of a range of copper-silicon alloys containing up to 8% silicon. Increasing the amount of silicon to 4% caused a gradual increase in the oxidation-resistance, while further additions up to 8% silicon decreased it. At 800° C. no sudden increase in the oxidation rate as found by Dunn at 827° C. was noted, although the maximum time investigated by Nishimura was 24 hr. and that of Dunn only 3 hr.

Copper-Aluminium.

Preston and Bircumshaw⁵² (ED) heated an aluminium bronze (7% aluminium + 4% manganese) in oxygen at 183° C. and obtained a diffraction pattern corresponding to Cu_2O . At 400° C. the outer layer of the surface film was thought to be MnO_2 . No evidence of crystalline Al_2O_3 was found.

According to Nishimura⁷⁵ (G) the addition of more than 2.0% manganese to a 10% aluminium bronze considerably decreases the oxidation-resistance in air at 700° C., although the same addition to a bronze containing 8% aluminium has very little effect.

Nishimura⁷⁵ (G) has also investigated the effect of nickel, iron, titanium, chromium, and arsenic on the oxidation of 8 and 10% aluminium bronzes at 700° C. in air. The effect of up to 1% arsenic,

1% chromium, 4% nickel, and 6% iron is negligible. Up to 6% titanium decreases the oxidation-resistance slightly. On a bronze containing 4% aluminium, the effect of more than 4% silicon was to decrease the oxidation-resistance considerably, although the effect of silicon on a bronze containing 6% aluminium was slight.

2. *Wagner's Theory of Oxidation and Selective Oxidation of Alloys.*

If Wagner's theory is correct, the electrical conductivity of the oxide film will influence the rate of oxidation to a very great degree, and oxides with low conductivities should produce films with high oxidation-resistance. Examination of Fröhlich's results (Table V) shows that the alloying elements giving the maximum oxidation-resistance are beryllium, aluminium, and magnesium. Price and Thomas⁸⁹ have quoted values for the electrical conductivities of the oxides formed by these elements and those giving lower oxidation-resistance, and it will be seen that the three elements giving the best oxidation-resistance also have oxides with the lowest conductivity (Table VII).

TABLE VII.—*Conductivity of Oxides of Elements in Table V at 1000° C. (Price and Thomas⁸⁹).*

Group	Oxide	Conductivity, mhos/cm.	Remarks
1	BeO Al ₂ O ₃ MgO	10 ⁻⁹ 10 ⁻⁷ 10 ⁻⁵
2	SnO ₂ * ZnO *	10 ⁻² 1	} Excess-cation type
3	SiO ₂	10 ⁻⁶	
4	TiO ₂ † CoO NiO CaO † FeO Fe ₂ O ₃	10 ⁻⁴ 10 10 ⁻² 10 ⁻⁷ 10 ⁻² 10 ⁻¹ Smaller volume than metal
5	CeO ₂ † Cr ₂ O ₃	10 ⁻² 10 ⁻¹
Cu (for comparison)	Cu ₂ O CuO	10 10	... Probably dissociates
Ag	Ag ₂ O	...	Dissociates

* High oxidation-resistance probably due to oxide being of excess-cation type.

† Element in question insoluble or only slightly soluble in Cu, and 2-phase alloy cannot be expected to have high oxidation-resistance.

Wagner³¹ has shown that where the electrical conductivity of the oxide film formed on a metal is independent of the oxygen pressure, and the controlling factor is a diffusion process, the constant K of the equation of oxide growth :

$$\frac{d\eta}{dt} = \frac{K}{y}$$

should be given by :

$$K = (n_1 + n_2)n_3cE_0/F.$$

where η = number of equivalents of oxide produced per cm.²
per sec.

t = time in seconds

y = thickness of film in cm.

F = Faraday's number

E_0 = affinity of the metal for oxygen in volts

n_1 , n_2 , and n_3 = the transport numbers of cations, anions, and electrons,
respectively, in the film,

and c = the specific conductivity of the oxide.

The value of $(n_1 + n_2)n_3c$ is shown by Wagner to be approximately 2×10^{-3} mhos/cm. for cuprous oxide at 1000° C. The value of $(n_1 + n_2)n_3$ for the passage of copper ions through alumina is not available, but the value can in no circumstances be greater than 0.25 (since $n_1 + n_2 + n_3 = 1$), while the value of c for alumina is about 10^{-7} mhos/cm. at 1000° C. The ratio of $(n_1 + n_2)n_3c$ for cuprous oxide and alumina must therefore be greater than :

$$\frac{2 \times 10^{-3}}{0.25 \times 10^{-7}}$$

i.e. greater than 80,000.

In other words, if sufficient aluminium is present in copper to cause the formation of an alumina film, the oxidation rate will be reduced by a factor of more than 80,000. Fröhlich, however, found that the addition of 2.5% aluminium to copper only decreased the oxidation rate by a factor of about 36. Price and Thomas⁸⁹ suggest that the reason for this discrepancy is that under natural conditions the alumina film that is formed contains veins or bridges of copper or Cu_2O which reduce its electrical resistance.

Price and Thomas therefore made experiments on a copper-5% aluminium alloy. Normal oxidation of this alloy for 4 hr. at 800° C. in dry oxygen produces a tenacious black oxide film. They considered that by carrying out the initial oxidation under conditions so slightly oxidizing that only alumina was formed, a much greater oxidation-

resistance could be obtained from this alloy. By heating first in moist hydrogen (0.1 mm. water-vapour pressure) for 15 min. at 800° C., and then exposing to full oxidizing conditions as mentioned above, they decreased the oxidation velocity by a factor of $\left[\frac{1358}{2.78}\right]^2 = 240,000$, a figure of the order predicted by Wagner's theory.

Hallowes and Voce⁶⁸ found that the selective oxidation of a copper-5% aluminium alloy by Price and Thomas's method protected it from atmospheric oxidation up to 800° C., provided that the film was not scratched or otherwise damaged. It did not confer protection against atmospheres containing SO₂ or HCl.

Price and Thomas⁸⁹ extended this technique to a copper-2.5% beryllium alloy, and considerable resistance to tarnishing was obtained by selective oxidation-treatment. Similarly, by electrolytic deposition of a film of BeO the tarnishing of copper at room temperature was almost prevented.⁹⁰

3. Internal Oxidation and Subscale Formation.

Copper-base alloys in which oxygen is relatively soluble may develop a subscale or zone of internal oxidation. Underneath the scale proper

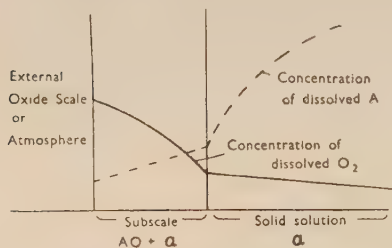


FIG. 6.—Concentration of Oxygen and Solute in a Solid Solution (*Rhines*⁷³).

is a layer consisting of copper with oxygen in solution and containing small particles of the oxide of the alloying element (see Fig. 6). This effect is due to the diffusion of oxygen into the alloy, resulting in preferential oxidation of the alloying element and its precipitation as an insoluble oxide.

As the solute is exhausted by precipitation, the oxygen supplied to the surface diffuses farther into the alloy and thus produces a subscale of ever-increasing thickness. Rhines^{74, 73} (*M*) and his co-workers have investigated subscale formation in a series of α solid solutions. Their work was mainly carried out at 600° and 1000° C., but alloys containing silicon, manganese, phosphorus, and aluminium were also investigated at 871° and 750° C. The duration of test was 2 hr. at 1000° C. and 192 hr. at 600° C. Alloys which formed subscales contained aluminium, arsenic, beryllium, cadmium, chromium, cobalt, iron, lead, manganese, nickel, phosphorus, silicon, selenium, tin, magnesium, and zinc, and also many other elements of less industrial

importance. Alloys containing silver, platinum, and palladium showed no internal oxidation. When a liquid phase was present, subscale formation was very much more rapid. Rhines found that the rate of growth of the subscale decreased with time, with increasing concentration of alloying element, and with reduction in the oxygen pressure.

Rhines and Nelson ⁸⁷ (*M*) have undertaken a comprehensive investigation on the structure of the subscale in the copper-zinc alloys oxidized at elevated temperatures. Subscale formation has also been noted by Smith ⁹¹ in copper-silicon alloys, by Hensel, Larsen, and Holt ⁷⁹ in copper-cobalt-silicon alloys, by Blazey ⁹² in copper containing bismuth and arsenic, and by Fröhlich.³⁵

Darken ⁹³ has discussed the mechanism of subscale formation and shown how the rate of growth and composition of subscale may be predicted from a knowledge of diffusion constants, phase relations, and boundary conditions.

The work of Rhines and his collaborators was summarized in 1947.⁹⁴ Rhines mentions in the course of his review, that the surface hardening of alloys due to the presence of finely distributed oxide does not seem to be possible. However, work carried out by Meijering and Druyvesteyn,^{95, 96} at about that time showed that such hardening is possible. Whereas the hardness of pure copper annealed in air at 950° C. is 50 V.P.N., the hardness of copper containing small amounts of either beryllium, magnesium, titanium, aluminium, or zirconium, was increased to the range 100–170 V.P.N. The maximum hardening effect (170 V.P.N.) was obtained with an addition of 0.2–0.35% beryllium. Amounts of aluminium exceeding 2.0% had no surface-hardening effect, while the addition of small amounts of either manganese, zinc, silicon, tin, or antimony had very little effect. In order to avoid loss by external oxidation, after a thin film of Cu₂O had been formed, diffusion was carried out in nitrogen or carbon dioxide.

The hardening mechanism appears to be similar to that of age-hardening, and the oxide particle-size must be sub-microscopic.

IV.—PRACTICAL ASPECTS OF OXIDATION OF COPPER AND COPPER ALLOYS.

The oxidation of copper and copper alloys is of considerable practical importance both in respect of the behaviour of materials in manufacture and in service, either at ordinary temperatures or at elevated temperatures.

From the published literature reviewed in the preceding section Table VIII has been compiled with a view to showing the extent of present knowledge of the types of scales formed on various copper-base

materials heated in air or oxygen at temperatures within or near the usual industrial range of annealing temperatures.

It is unfortunate that little information is available on the thickness of films formed within the normal annealing range, viz.: 400°–600° C. The majority of investigators have carried out work at temperatures

TABLE VIII.—*Summary of Data for Oxide-Growth Constant (K) for Copper and Copper Alloys Heated in Dry Air or Oxygen at Atmospheric Pressure.*

Material	Temperature, °C.	$K, \text{g.}^2 \text{cm.}^{-4} \text{hr.}^{-1}$	Nature of Film	Ref. No.
Tough-pitch copper	400	5.8×10^{-8}	} Exfoliative	63
Tough-pitch arsenical copper . .	400	1.8×10^{-8}		
Phosphorus-deoxidized copper . .	400	2.9×10^{-8}		
Phosphorus-deoxidized arsenical copper	400	1.3×10^{-8}		
Tough-pitch copper + 1% Ag . . .	400	5.8×10^{-8}	} Exfoliative	63
„ + 1% Cd	400	0.35×10^{-8}		
Brass (70 : 30)	580	8.8×10^{-9}	Partly adherent	84
„ (60 : 40)	580	5.5×10^{-9}	} Adherent	84
„ (60 : 40)	425	2.2×10^{-10}		43
Al brass (70 : 30 : 2)	775	1.3×10^{-10}	Adherent	84
Bronze (2.8% Sn)	800	2.1×10^{-5}	...	} 35
„ (8.6% Sn)	800	1.5×10^{-6}	...	
„ (6.1% Sn, 0.54% P)	800	2.1×10^{-5}	...	
„ (5.0% Sn, 0.11% P)	400	2.3×10^{-8}	Slightly adherent	
Al bronze (7% Al)	400	$<1 \times 10^{-11}$	Adherent	63
„ (10% Al, 5.0% Fe, 5.0% Ni)	400	$<1 \times 10^{-11}$	„	63
Si bronze (3% Si, 1.0% Mn) . . .	400	8.0×10^{-9}	Fairly adherent	63
„ (3% Si)	800	6.0×10^{-6}	...	35
Cupro-nickel (30% Ni)	800	7.5×10^{-5}	...	81
Cu-Ni-Si (0.75% Ni, 0.5% Si) . .	400	6.0×10^{-9}	Exfoliative	63

of 700°–1000° C. Most of the information given for 400° C. was obtained by alternate oxidation and scale removal.

By means of the rate constant (K) for any particular alloy and temperature, an estimate of the thickness of the oxide film * formed in air may be obtained from the following formula :

Thickness of scale formed in 1 hr. = $1.5\sqrt{K}$ cm.
where K = rate constant ($\text{g.}^2 \text{cm.}^{-4} \text{hr.}^{-1}$).

* It is assumed that the oxide is Cu_2O or CuO . These will form the bulk of the scale on most copper-base alloys heated in atmospheres rich in oxygen.

As has already been mentioned, when the logarithms of the rate constants are plotted against the reciprocals of the absolute temperatures, a straight line, or in the case of copper two straight lines, will result. It is perhaps unfortunate that these two lines formed in the case of copper (and copper containing small amounts of some other elements), intersect within the annealing range, i.e. at about 580° C., but sufficient information is available for this material to be able to calculate the film thickness at any temperature (see Fig. 3).

The only alloy for which there is sufficient data to be able to obtain a complete plot of $\log K$ against $1/T$ over the whole range of temperature is a 60 : 40 brass (Fig. 7). In this case the intersection of the two straight lines occurs outside the normal annealing range, i.e. at about 300° C.

However, while the above procedure can give an idea of the thickness of scale produced by an annealing treatment in air, further data is required to calculate the thickness of films formed in bright-annealing atmospheres. For copper for a given time the film thickness will be proportional to the partial pressure of the oxygen present up to a certain critical pressure, after which it varies only slightly with the oxygen pressure (according to the results obtained by Pilling and Bedworth¹⁹ (Fig. 4) and Wagner and Grünewald.²² The pressure above which the oxidation rate varies only slightly with pressure, depends on the surface finish, but with rolled surfaces is likely to be less than 0.3 mm. (Hg).

The oxygen partial pressure of the atmospheres used, other than for cracked ammonia which is reducing, will probably be less than this value, and therefore the oxidizing properties will vary considerably with gas composition, as the relevant part of the curve in Fig. 4 will be the very steep portion. The exact composition of the atmosphere, i.e. whether impurities are present such as HCl, H₂S, or H₂O, &c., will have a marked effect on the scaling behaviour in these atmospheres. The presence of all these impurities can, of course, be avoided, but in industrial annealing practice this is rarely economic, and large fluctuations are to be expected.

Pawlek⁹⁷ has investigated the effect of bright-annealing atmo-

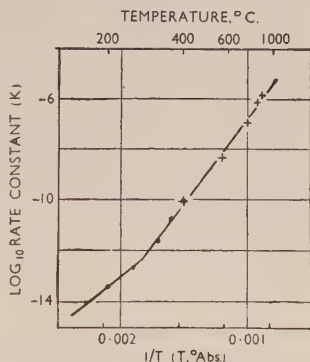


FIG. 7.—Oxidation Rate of 60 : 40 Brass in Air and Oxygen.

KEY.

- + Dunn⁸⁴ (in oxygen).
- Vernon⁴² (in air).

spheres on copper and copper-base alloys. The atmospheres covered include partially burnt cracked ammonia, burnt town's gas, and burnt propane, with various ratios of air : gas, and also a vacuum. The effect of annealing copper and the following alloys is shown by means of colour photographs : 5-6% aluminium bronzes, brasses (10-40% zinc), cupro-nickel (78% copper-22% nickel), and aluminium brasses. The effect of the sulphur present in the propane is of particular importance.

Probably the most important property of a scale to the manufacturer of copper-base alloys is its adherence. This property has so far had very little attention according to the literature. Generally a thick scale tends to exfoliate while a thin scale is normally adherent, but there is no doubt that small amounts of alloying elements may exert a marked effect on the property of adherence without affecting the thickness of the film. For example, the presence of 0.47% arsenic makes little or no difference to the rate of oxidation of copper in dry air,⁴² but this element helps to give an adherent scale in a firebox atmosphere at low temperatures.

Bamford⁹⁸ noted that tough-pitch non-arsenical copper had a very adherent scale which did not flake off on air-cooling from 750° C., and penetrated into the metal (i.e. formed a thick subscale). The addition of 0.45% arsenic was found to obviate this, and the scale was more easily removed. It will be noted that this appears to conflict to some extent with Hudson's results⁴² quoted above.

The effect of heat-treatment and cooling rates on the adherence of scales on different types of copper has been investigated by Webster,^{99,100} and his co-workers. The first part of the work⁹⁹ was carried out by slowly heating pieces of 1½-in.-dia. tube in two grades of copper : phosphorus-deoxidized (0.009% phosphorus (P.D.O.)) and tough-pitch (Lake) (T.P.). Pieces of each grade were withdrawn at intervals of 100°, from 450° C. upwards, and quenched. At 450° C., after quenching, both coppers had a mottled appearance. Between 550° and 750° C. the scales were completely removed from both coppers. At 850° C. that on P.D.O. was completely removed, while only 5% of that on the T.P. copper was removed. After quenching, the specimens of T.P. were all red, while those of P.D.O. were red to pink. The heating time varied from 17 min. at 450° C. to 88 min. at 850° C.

The second part of the work¹⁰⁰ consisted of annealing the coppers for ½ hr. at temperatures between 500° and 900° C., and either removing the scale by pickling or quenching. An O.F.H.C. copper was added to the series for comparison. The results of quenching were very much the same as those obtained in the previous experiment. In the case of the T.P. and O.F.H.C. coppers, the scale was partially adherent at 800° C.,

and almost completely adherent at 900° C. In the case of the P.D.O. copper, the scale was completely removed at 800° and 900° C. The scale of all three coppers was removed by pickling after annealing at all temperatures.

These results show that the effect of adding phosphorus to the copper influences the adherence between the scale and the metal, which the presence of oxygen in the metal does not do.

Sharavsky ¹⁰¹ investigated the effect of small amounts of impurities on the adherence of cuprous oxide films formed on copper at 1000° C. The specimens were taken out of the furnace at 1000° C., and placed in another at 600° C. and furnace-cooled to room temperature. It was found that the elements aluminium, beryllium, silicon, nickel, arsenic, tin, and antimony produced non-adherent scales if the concentration was high enough. The presence of small amounts of silver, phosphorus, manganese, iron, cobalt, zinc, cadmium, gold, thallium, and lead did not have this effect.

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THE ADHERENCE OF OXIDE SCALES ON 1281 COPPER.*

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WITH AN APPENDIX ON THE TEMPERATURE OF THE OXIDE SCALE ON COPPER DURING HOT ROLLING.

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

The scales formed on pure or tough-pitch copper and on phosphorus-deoxidized copper are known to behave very differently during fabrication, the phosphorus-bearing coppers shedding their scales more readily than the phosphorus-free coppers during hot working. A corresponding difference is observed in laboratory tests when specimens are oxidized in air at hot-working temperatures and then cooled to room temperature, the phosphorus-bearing coppers shedding their scales freely on cooling, while the scales on phosphorus-free coppers remain strongly adherent. These differences in scaling behaviour are explained in terms of the mechanical properties of the scales at elevated temperatures. The oxide scales on copper, consisting largely of cuprous oxide, are remarkably ductile at elevated temperatures. For example, wire specimens consisting entirely of oxide extend about 20% before fracture under tensile stress at 700°–900° C., the ductility decreasing with decrease of temperature to about 5% elongation at 300° C. The scales on coppers containing phosphorus, on the other hand, have very limited ductility, never exceeding about 5% elongation over the whole temperature range, and they are therefore unable to accommodate the plastic strains imposed on them by hot-working operations or by the differential contraction of metal and scale when the oxidized copper cools to room temperature. The hot shortness of these scales is due to intergranular films of a molten phase, probably a cuprous phosphate.

In the Appendix an estimate is made of the temperatures reached by the oxide scales when a slab preheated to 900° C. is passed through the rolls. It is shown that the scale rapidly cools to a temperature at which the ductility of the scale on phosphorus-free copper is fairly strongly dependent on the temperature, and it may be inferred that moderate reductions in initial slab temperature would markedly favour exfoliation of the scale.

I.—INTRODUCTION.

IN the fabrication of copper and copper alloys difficulties are sometimes caused by adherent oxide scales formed on the materials during pre-

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heating before hot working or during annealing before cold working. There is a wealth of information in the literature on the rates at which copper and its alloys oxidize in various environments, but practically nothing is known of the characteristics which govern the adherence of the oxide scales to the basis metals, and the present work was undertaken to provide such information.

The scaling of pure copper, oxygen-bearing copper, and phosphorus-bearing copper has been studied in detail, largely because these materials are known to behave differently in practice, phosphorus-deoxidized coppers tending to shed their scales more readily than phosphorus-free coppers after preheating for hot working. The scaling of arsenical tough-pitch copper was also examined, but in less detail because preliminary laboratory tests revealed scaling characteristics somewhat similar to those of deoxidized copper.

The adherence of the oxide scales formed on these materials was determined by observing the exfoliation of the scales during cooling and by deforming oxidized specimens at elevated temperatures. Explanations for the observed differences in adherence were sought by mechanical tests on the bulk scales at elevated temperatures and by metallographic examination of the scales after cooling.

The probable behaviour of the scales when the oxidized materials are hot worked is discussed in the light of the results of the laboratory tests, and in this connection an estimate of the temperature attained by the scale during the hot rolling of a copper slab is given in an Appendix to the paper.

II.—MATERIALS AND GAS ATMOSPHERES.

1. *Coppers Examined.*

The following details apply to all the work; but it is convenient to give other details of experimental methods later, together with the results. The compositions of the materials used are given in Table I.

The specially refined coppers (triple electrolytic process) were melted and cast *in vacuo*, with and without the phosphorus additions indicated in Table I. The tough-pitch coppers were cast from large commercial melts, and the deoxidized (CCC brand) copper was made from the corresponding tough-pitch material by remelting in a Salamander crucible under charcoal and adding phosphorus.

2. *Preparation of Specimens.*

The materials were cold drawn to $\frac{5}{16}$ in. dia. rods. With the exception of the arsenical copper, they were pickled immediately before the final draw, then drawn without lubricant and stored in desiccators.

These rods were cut to length and the ends machined immediately before use. No surface preparation was given other than degreasing with acetone. The arsenical copper was also obtained in the form of $\frac{5}{16}$ in. dia. rod, but lubricant was used throughout drawing. The material was lightly pickled in warm 10% sulphuric acid for 15 sec., washed and dried carefully, washed in acetone and dried again before use.

TABLE I.—*Analysis (Wt. %) and Types of Coppers.*

Element	Lower Limit of Detection	Specially Refined (1st batch)		Specially Refined (2nd batch)		CCC Brand		Arsenical Tough-Pitch
		NPV ("Pure")	NPW (0.04% P)	NTB, NTC, NTE ("Pure")	NTF (0.03% P)	NPE (Tough-pitch)	NPF (Phosphorus-deoxidized)	OCA, OCB
Oxygen *	0.0001	0.0001	0.0001	0.0001	0.0002	0.030	0.002	0.045
Silver	0.0005	0.001	0.001	0.0005	0.0005	<0.0005	<0.0005	0.004
Phosphorus *	—	nil	0.038	nil	0.030	nil	0.034	nil
Nickel	0.0001	0.0005	0.0005	0.0001	0.0001	0.0005	0.0005	0.05 *
Iron	0.0001	0.0002	0.0002	0.0002	0.0002	0.0005	0.0005	0.001
Lead	0.0002	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.005
Antimony	0.0002	<0.0002	<0.0002	0.0002	0.0002	<0.0002	<0.0002	0.002
Arsenic	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.44 *

* By chemical analysis, rest spectrographic.

The specimens used for the exfoliation tests were 7 cm. long (2.76 in.) and 0.8 cm. (0.31 in.) in dia. A hole $\frac{1}{16}$ in. in dia. was drilled transversely near one end for attachment to a suspension wire and for the insertion of a thermocouple. The surface area of this specimen was 18.4 cm.² The specimens for the torsion test described later were 14 cm. long and had transverse holes drilled 0.8 cm. from either end.

3. Purification of Gas Atmospheres.

Nitrogen was purified by passing it through alkaline pyrogallol, and was dried with calcium chloride and phosphorus pentoxide. Air was obtained from a compressed-air cylinder, and was passed over potassium hydroxide and phosphorus pentoxide.

III.—EXFOLIATION OF SCALE DURING COOLING.

Simple tests were carried out to determine the degree to which scales on the different types of copper exfoliate during cooling after oxidation at various temperatures for times of 1, 2, and 4 hr. Estimates were also made of the temperature at which exfoliation started during cooling.

Exfoliation under these conditions is largely due to stresses caused by differential thermal contraction. For oxide scales on copper and the dilute copper alloys studied, the difference between the thermal expansion coefficients of metal and scale is large, the values being 17×10^{-6} and $0.93 \times 10^{-6}/^{\circ}\text{C.}$ for copper and cuprous oxide, respectively. The oxide film is thus compressed on cooling. For a flat plate, large in comparison with the thickness of the film, a two-dimensional compressive stress is produced. If the film is initially stress-free and not plastic, the stresses are proportional to the fall in temperature. They must become large for a quite moderate fall in temperature, since the difference in expansion amounts to 0.16% for each 100°C. In practice there may well be additional stresses, produced during formation of the film. It can be shown that, except at the edges of the plate, there is no stress at the interface unless the film fails or unless it starts to buckle away from the surface.* With a bar, however, as used in these experiments, conditions are more complicated, since the radial shrinkage of the bar and the compressive stress in the film impose a tensile stress normal to the interface. It would therefore be expected that the scale on a bar would exfoliate rather more readily than that on a plate.

1. *Test Method.*

In most of the tests the specimens were suspended four at a time in a vertical tube furnace of $2\frac{1}{2}$ in. dia., with thermocouples attached to each specimen. The arsenical copper specimens were oxidized one at a time in a $1\frac{1}{4}$ in. dia. tube furnace. The specimens were brought to temperature in an atmosphere of nitrogen, purified as described earlier, and purified air was then substituted. The rate of flow was 64 l./hr. for the large furnace and 32 l./hr. for the small one. After oxidation the specimens were removed from the furnace, with thermocouples attached, and each was suspended in a separate Pyrex glass test-tube so that the temperature at which exfoliation started could be observed.

The exfoliated scale collected in each tube was weighed, and attempts were made by various methods to calculate the percentage of scale exfoliated. None of these was entirely successful, and since the main features of the results were brought out equally well by visual observations of the amount of exfoliation, only these observations are reported. They refer only to the outer layer of the scale and do not preclude the retention, on specimens for which complete exfoliation is reported, of a substantial layer of inner scale.

* This statement is strictly true only of large-scale forces and in the elastic range. More generally, effects of the type recently considered by Frank and van der Merwe,¹ involving the formation of dislocations at the surface and associated small-scale stresses, would have to be taken into account.

2. Results.

The percentages (obtained by X-ray methods) of cupric oxide in the scales formed in air at various temperatures are given in Table II; except for the very low values at the highest temperatures, there is no regular trend, and the variations would appear to be fortuitous. Table III lists the exfoliation temperatures and visual estimates of the amounts of exfoliation after oxidation at various temperatures. Corresponding data for the subsequent experiments on arsenical tough-pitch copper are given in Table IV.

TABLE II.—Composition (% CuO) of Scales formed on “Pure”, Tough-Pitch, and Phosphorus-Containing Coppers.

Oxidation Temperature, ° C.	“ Pure ” Copper (NTB)	Copper+0.03% Phosphorus (NTF)	Tough-pitch Copper (NPE)	Phosphorus-Deoxidized Copper (NPF)		
	Oxidation Time					
	1 hr.	1 hr.	1 hr.	1 hr.	2 hr.	4 hr
900	5	1	Not detected 2-5	15
800	10	25		32	20	25
700	35	20		25
600	10	15		35
500	25	65		35	65	35
400	45	35	25	35

Accuracy $\pm 5\%$ when 10% or more of CuO present.

Table III shows that the behaviour of tough-pitch and oxygen-free copper is substantially the same. The scales formed at 400° C. are semi-adherent, those formed at 500° C. are non-adherent, and with higher temperatures of oxidation the scales become progressively more adherent, being completely adherent when formed at 800° and 900° C. The exfoliation temperatures recorded in Table III range up to 530° C. It is shown in Section IV that at temperatures a little above this the scales, particularly on phosphorus-free copper, are quite plastic, so that the stresses which cause the film to exfoliate probably cannot be built up at higher temperatures.

Experiments were also carried out at 800° and 900° C. on coppers NTE and NPE, which normally have adherent scales, to see whether the addition of 0.1% sulphur dioxide to the air atmosphere had any effect on oxidation and scaling. The oxidation rate was unaltered, and no change in the adherence of the scales was observed.

TABLE III.—*Amounts of Exfoliation (Visual Estimates) and Exfoliation Temperatures.*

Type of Copper	Oxidation Temperature, °C.	Oxidation Time					
		1 hr.		2 hr.		4 hr.	
		Exfoliation					
		Amount	Temp., ° C.	Amount	Temp., ° C.	Amount	Temp., ° C.
“ Pure ” (NTB)	900	Nil	...	Nil	...	Nil	...
	800	” Complete	500	” Partial Complete	200	” Partial	95
	700		270		Not observed		
	600	”	*	”	Complete	”	
	500	” Partial	430	”	350	”	”
	400		150		290		”
Copper + 0.03% Phosphorus (NTP)	900	Complete	340	Partial	Not observed	Complete	270
	800	”	290	Complete	500	”	415
	700	”	520	”	Not observed	”	270
	600	”	450	”	360	”	Not observed
	500	”	240	Partial	200	”	”
	400	”	130	”	Not observed	”	375
Tough-pitch (NPE)	900	Nil	...	Nil	...	Nil	190
	800	” Complete	530	” Complete	Not observed	” Partial	200
	700		”		”		100
	600	”	*	”	”	300	
	500	” Partial	430	”	”	Complete	Not observed
	400		200		”		”
Phosphorus-Deoxidized (NPF)	900	Partial	340	Partial	Not observed	Complete	500
	800	Complete	370	Complete	”	”	490
	700	”	320	”	”	”	330
	600	”	440	”	330	”	Not observed
	500	”	310	”	320	”	”
	400	”	Not observed	”	160	”	”

* Scale exfoliated in one piece, so that it was impossible to observe exfoliation temperature.

The scales formed on the coppers containing phosphorus were all substantially non-adherent for all temperatures of oxidation.

The behaviour of arsenical copper is somewhat similar to that of copper containing phosphorus, but the scale is rather more adherent, both the exfoliation temperatures and the percentages of exfoliation being somewhat lower (Table IV). The amounts of oxygen absorbed by the arsenical copper specimens were the same as for the other coppers at 800° C. and below; at 900° C. the arsenical specimens absorbed about 50% more oxygen than the other coppers.

TABLE IV.—*Scaling of Arsenical Copper (OCB).* $\frac{5}{16}$ in. dia. specimen; area = 18.4 cm.²; surface: flash-pickled.

Oxidation Temperature, ° C.	Oxidation Time, hr.	Exfoliation	
		Amount	Temperature, ° C.
900	1	Complete	170–20
	4	„	175
800	1	Complete	125
	4	„	100
700	1	Partial	100
	4	„	100–150
600	1	Partial	300
	2	„	375
	4	Complete	400–150

IV.—ADHERENCE OF SCALES UNDER WORKING CONDITIONS.

When copper and copper alloys are hot worked in practice the metal and scaled surface are subjected to severe deformation. Notwithstanding this, it is known that the scale on certain materials remains strongly adherent, and to assess this characteristic a hot-torsion test was employed which permits the imposition of large and uniform strains.

Two procedures were used. In the first the cylindrical rods were heated for 1 hr. at temperatures in the range 950°–400° C. and then twisted. In the second, the bars were oxidized at 900° C. for 1 and 4 hr., respectively, and allowed to cool to testing temperatures in the range 800°–400° C. The first type of test should indicate the mechanical properties of the scales at the temperature of formation, while the second test should indicate the behaviour of scales such as those formed in a preheating furnace and then subjected to hot working, as for example in the breaking-down of a wire bar.

1. *Hot-Torsion Test Apparatus and Method.*

The ends of the cylindrical test-bar were gripped in two Inconel tubes, one of which was fixed, while the other could be rotated through a measured angle (Fig. 1). This assembly was placed in a horizontal Inconel tube furnace, the interior of which could be viewed, at its mid-length, through a side branch projecting through the furnace casing, closed with a window and provided with a platinum filament for illumination (see Fig. 2). The provision of this viewing tube resulted in an uneven temperature in the specimen, the ends being hotter than

the middle, but this was minimized by inserting copper rods in the Inconel tubes holding the specimen so that heat was conducted away from the ends of the specimen. In this way the temperature of the centre section of the specimen was brought to within 13°C . of the hottest parts (midway between ends and centre) and the test temperatures recorded are mean values measured at a point 1.4 cm. from the end of the specimen.

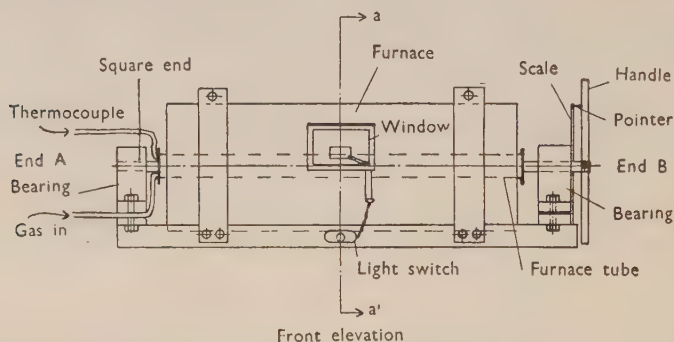


FIG. 1.—Hot-Torsion Test Apparatus.

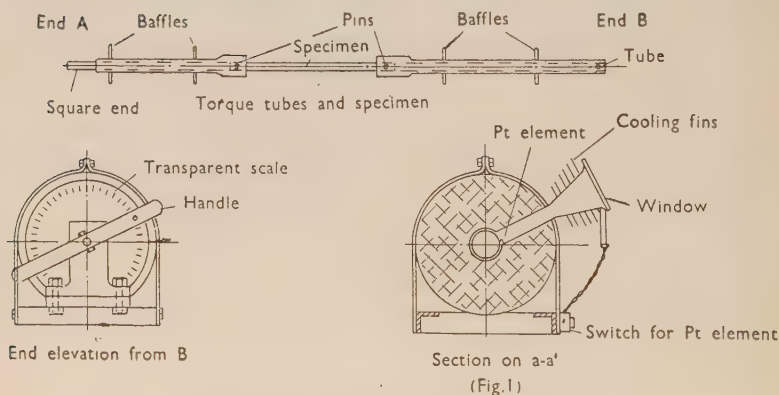


FIG. 2.—Details of Hot-Torsion Test.

Specimens were raised to test temperature in an atmosphere of purified nitrogen. No visible oxidation of the specimens occurred in the heating-up period. When the specimen was at temperature, dry air was admitted and a black film appeared on the specimen within 1 min. at all temperatures of test. After oxidizing for the required time, the specimen was twisted and the behaviour of the scale was noted.

To interpret the results of the test, it is necessary to consider the

stress system set up in the scale on the surface of a bar submitted to a torsional strain. If the bar is fixed at end *a* (Fig. 3) and twisted clockwise at end *b*, a small square element of the surface is subject to pure shear stresses as shown. The principal compressive and tensile stresses are parallel to the diagonals *AC* and *DB*, respectively, and are both equal to the shear stress.

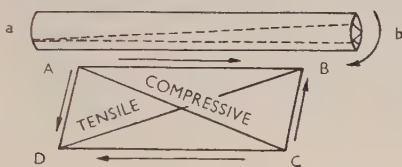


FIG. 3.—Compressive and Tensile Stresses in Strained Bar.

Failure of the scale will either occur along lines perpendicular to direction *BD*, owing to the principal tensile stress causing tensile failure of the scale, or perpendicular to *AC*, owing to the compressive stress tending to buckle the scale and break its adherence with the parent metal. Examples of compressive and tensile failure are given in Fig. 4 (*a*), (*b*), and (*c*) (Plate XXXV).

The actual shear strain imparted to the surface is

$$\frac{r\theta}{L}$$

where *r* = radius of bar, θ = angle of twist (in radians), and *L* = length. For the bars used (0.8 cm. dia. and 12.4 cm. effective length), the shear strain = 0.032 θ .

2. Results.

Reference to Table V, which gives the results of tests on specimens oxidized for 1 hr. at the test temperature, shows that scales on phosphorus-free coppers are extremely ductile when formed and tested at temperatures between 950° and 700° C. These scales neither buckled nor cracked in any test, although the shear strain was in some tests as much as 0.9, equivalent to about 4½ turns of the specimen. With oxidation temperatures of 600° C. or lower the scales cracked at small angles of twist.

The scales on the two kinds of phosphorus-bearing coppers behave differently, but in each case are comparatively brittle at some temperatures between 700° and 950° C. The scales formed at 700° and 800° C. on the specially refined copper with added phosphorus withstand large deformations, but those formed at 900° and 950° C. are much less plastic. On the other hand, the scales formed at 700° and 800° C. on

the deoxidized copper fail by buckling or cracking at small deformations, though at 900° and 950° C. the scales are more plastic. All scales formed at about 600° C. and below are uniformly brittle, irrespective of the nature of the basis material.

TABLE V.—*Effect of Twisting on Scales Formed on "Pure", Tough-Pitch, and Phosphorus-Containing Copper after Oxidation for 1 hr. (Shear Strain to Failure *).*

Oxidation Temperature, ° C.	“ Pure ” Copper (NTB)		Copper + 0.03% Phosphorus (NTF)		Tough-Pitch Copper (NPE)		Deoxidized Copper (NPF)	
	Strain to :							
	Buckle	Crack	Buckle	Crack	Buckle	Crack	Buckle	Crack
950	>0.7	>0.7	...	0.29	>0.9	>0.9	0.65	0.65
900	>0.6	>0.6	0.27	0.7	>0.8	>0.8	0.68	>0.7
800	>0.6	>0.6	0.65	>0.8	>1.0	>1.0	0.10	0.45
700	>0.6	>0.6	>0.6	>0.6	>0.8	>0.8	0.02	0.26
600	...	0.01	...	0.006	...	0.010	...	0.02
500	...	0.01	0.01	0.01	...	0.003	0.02	0.02
400	0.02	0.02	0.01	0.01	...	0.006	<0 †	0.03

* First crack or buckle.

† Buckled during formation.

The torsion-test specimens of the phosphorus-free coppers, oxidized and twisted at 950°–800° C., invariably exfoliated during cooling at low temperatures (about 250° C.). This may indicate that the bond between metal and scale had been weakened, or that internal stress or work-hardening had been produced in the scales by the deformation, since such scales not subjected to strain are adherent at room temperature.

TABLE VI.—*Effect of Twisting on Scales formed by Heating at 900° C. for 1 hr. and Cooled to Twisting Temperature (Shear Strain to Failure *).*

Twisting Temperature, ° C.	"Pure" Copper (NTE)	Copper + 0.03% Phosphorus (NTF)	Tough-Pitch Copper (NPE)	Deoxidized Copper (NPF)
800	>0.7	0.17	>0.8	0.06
700	>0.8	0.20	>0.8	0.1 (0.013)
600	>0.7	0.026	0.55	0.05
500	0.07	0.006	0.26	0.003
400	0.08	0.006	0.055	0.003

* First crack or buckle.

The behaviour of scales formed by oxidation for 1 hr. at 900° C., and then cooled to various lower temperatures before twisting, is shown in

Table VI. A slight difference in behaviour, compared with the scales formed at the test temperature, is shown by the specially refined copper with added phosphorus. The scales formed at 900° C. withstand smaller deformation at 700° and 800° C. than do the scales formed and tested at these temperatures (cf. Tables V and VI). This difference could be attributed to the strains already imposed on the scale during cooling. A difference in the opposite sense is shown by the scales on coppers without phosphorus, which in this test have greatly increased ductility at 600° C. and still retain some ductility at lower temperatures. This can only be due to a real difference in the properties of the scales, perhaps because the thicker films can withstand a higher compressive stress before failure (i.e. they behave somewhat like a strut in compression).

Although the differences in behaviour are ascribed above to differences in ductility, there is, of course, no clear distinction in these tests between failure of the scale in bulk and failure of the interfacial bond; this matter will be discussed later.

The results of the torsion tests correlate well with those of the exfoliation tests. For example, the scales formed on phosphorus-free coppers at temperatures from 400° to 600° C. show little ductility in the torsion test and exfoliate readily on cooling, whereas those formed at 900° C. are extraordinarily ductile down to 600° C. and still retain some ductility at the lowest temperatures of test. Other parallels may readily be found in the tables.

TABLE VII.—*Results of Torsion Tests on Tough-Pitch Arsenical Copper (OCB).*

Rod dia. 8 mm.; effective length 12.6 cm.

Oxidation or Twisting Temperature, ° C.	Twisted after 1 hr. at Temperature, °C.	Oxidized 1 hr. at 900° C. and Cooled to Twisting Temp.	Oxidized 4 hr. at 900° C. and Cooled to Twisting Temp.
	Shear Strain to Failure		
900	>0.61	>0.61	>0.61
800	>0.52	>0.52	>0.48
700	>0.45	>0.42	>0.52
600	0.019	>0.42	0.45
500	0.016	0.32	0.11
400	0.011	0.16	0.016

The results of the torsion tests on tough-pitch arsenical copper are given in Table VII. It was not possible to twist this material through the extremely large angles used for "pure", tough-pitch, and

phosphorus-containing coppers, since the rods themselves tended to fail with twists of between 2 and 3 turns, (shear strain in scale 0.4 — 0.6). It appears that in the torsion test the scales behave rather similarly to those of "pure" and tough-pitch coppers, although in the exfoliation tests they were intermediate between the scales formed on the phosphorus-free and phosphorus-containing coppers. Moreover, there is a marked difference in behaviour at 500° and 400° C. between the scales formed at 900° C. in 1 hr. and in 4 hr., respectively. These results suggest that in this case the scaling behaviour may not depend so much on bulk properties, and that the conditions at the interface may be more important.

V.—BULK PROPERTIES OF SCALES.

In view of the results quoted, it was clear that a knowledge of the bulk properties of the scales was required. A series of tensile tests were therefore carried out at elevated temperatures on specimens of typical 900° C. scales in the form of wires.

1. *Test Method.*

Rods of three coppers, "pure" copper (NTB), copper +0.03% phosphorus (NTF), and tough-pitch arsenical copper (OCA), were drawn down to wires 0.020 in. in dia.

For each test a length of wire 4 in. long was joined at the ends with interlocking loops to lengths of nickel-chromium wire (0.048 in. dia.), and the whole suspended in a vertical tube furnace from a fixed support. The bottom length of nickel-chromium wire terminated in a hook to which a pan could be attached. The copper wire was oxidized at 900° C. until the entire gauge-length was just converted to oxide. This stage was determined by measuring the electrical resistance of the test wire and part of the nickel-chromium end wires. It was found that hardly any change of resistance occurred in the first 1½–2 hr. of oxidation in the case of the "pure" and phosphorus-containing coppers; after this there was a very rapid increase of resistance lasting about ½ hr., up to a point where no further change took place. The rapid increase began when the wire was oxidized completely at the centre of the gauge-length and finished when complete oxidation had extended to the ends. The oxidation temperature was measured by means of a thermocouple attached to the junction of the copper wire and the top nickel-chromium supporting wire. Owing to the higher oxidation rate of the arsenical copper, the time taken for complete oxidation of the wire was only about 1 hr.

When the wires were heated up, oxidized, and cooled to room temper-

ature, there was an increase in length of 2%. The elongation at fracture under stress was therefore obtained by reference to the original length of the wire, and a deduction of 2% was made to allow for this growth.

There was an increase in the diameter of the wire due to its conversion to oxide of lower density. The diameters of oxide wires before stressing, and the corresponding specific gravities were as follows :

	Dia. of Oxide Wire, in.	Specific Gravity
"Pure" Copper (NTB)	0.026	5.6
Copper +0.03% phosphorus (NTF)	0.028	4.9
Tough-Pitch Arsenical copper (OCA)	0.027	5.6

The specific gravity for cuprous oxide given in the International Critical Tables varies from 5.80 to 6.05, and that for cupric oxide is 6.2. The reason for the lower figures shown above is undoubtedly due to there being considerable porosity in the specimens (see Figs. 5-8, Plates XXXVI and XXXVII), which is greatest for the copper containing phosphorus (NTF) (Fig. 7).

During oxidation the bottom supporting wire was clamped to avoid its weight (17 g.) being applied to the specimen during oxidation. When the copper wires were completely oxidized and had been cooled to testing temperature, a pan weighing 98 g. was attached to the hook on the bottom supporting wire and the pan was loaded with sand. The specimens were broken in about 15 sec.

The only difficulty encountered in the use of this test was keeping the gauge-length perfectly straight before application of load. If the wire were slightly bent, a bending moment would be applied. Bending of the wire would be of no importance where the wires had some ductility, but where they were brittle, slight bending would lead to failure at low loads. This is presumed to be the reason for the apparent loss of strength at low temperatures and occasional low values at higher temperatures on the less ductile specimens.

2. Results.

The results of these experiments are given in Fig. 22. It will be seen that the oxide of the copper (NTB) is moderately ductile at 500°-600° C. (12% elongation) and extremely ductile at 700°-900° C. (25% elongation), while the elongation of the oxides from the phosphorus and arsenical coppers never exceeded 5% for the whole range.* The

* The elongation found appears to be predominantly due to plastic, rather than viscous, extension, since substantially similar results are obtained at different rates of loading, as is indicated by the following results on copper (NTB) at 700° C. :

Loading Time	U.T.S., lb./in.*	Elongation at Fracture, %
15 sec.	3080	16
7 min.	3510	25

specimens of oxide from the copper (NTB) showed considerable local elongation or necking when pulled at 800° and 700° C. The majority of specimens from this copper showed general reduction in area throughout the gauge-length.

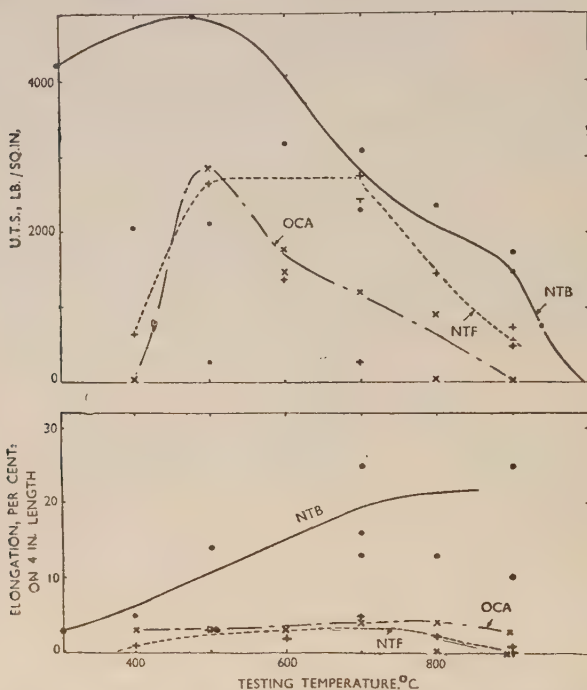


FIG. 22.—Properties of Copper Wires Completely Oxidized at 900° C. and Cooled to Testing Temperature.

- Copper (NTB).
- + Copper + 0.03% phosphorus (NTF).
- × Tough-pitch arsenical copper (OCA).

The strengths of these oxides, which reach a maximum of about 3000–5000 lb./in.² at 500°–600° C., seems remarkable. It explains the force with which the oxide is ejected from the underlying parent metal during the exfoliation tests. The ductility of the oxide from the “pure” copper accounts for its ability to withstand severe deformation at temperatures above 500° C.

The ductility of scales from arsenical copper is similar to that of copper containing phosphorus, in agreement with the exfoliation tests, but it is difficult to reconcile these low values with the results of the torsion tests. The oxides from the other two coppers, however, have

properties which adequately account for their behaviour in the torsion test.

VI.—CONSTITUTION AND MICROSTRUCTURE OF COPPER OXIDE SCALES.

1. *Composition of Scales.*

As is well known, the scales formed on copper consist substantially of cuprous and cupric oxide, and the percentages of cupric oxide formed under different conditions have already been given in Table II. These results were perforce obtained after cooling to room temperature, and it is possible, especially with the scales which exfoliated on cooling (all except those formed on phosphorus-free coppers at 800° and 900° C.), that some conversion from cuprous to cupric oxide occurred on cooling, leading to somewhat high figures for cupric oxide content. The figures on the whole seem to vary rather unsystematically, the only noteworthy feature being the small amount of cupric oxide formed at 900° C. and in one case at 800° C. This result appears to be in line with the decreased stability of cupric oxide at high temperatures.

Scales formed on a copper containing 0.1% phosphorus at 800° and 900° C. in 1 hr. were found to contain about 0.08% phosphorus. This means that, when due allowance is made for the oxygen content of the scale, the ratio of phosphorus to copper in the scale is about the same as in the metal. The scale formed at 800° C. in 1 hr. on arsenical copper (0.45% arsenic), however, contained only 0.25–0.32% arsenic compared with the expected value of about 0.39%, so that there may be a slight loss of arsenic by volatilization.

Of more importance than the quantity of phosphorus and arsenic present in the film, is the manner in which they are distributed, whether dissolved in the copper oxides or as separate phases, and if they occur as separate phases, what the distribution and characteristics of the phases are.

2. *Preparation of Sections.*

The specimens were held in position on a glass slide with the oxidized face vertical. A 1 in. dia. stainless steel ring was placed round them and fixed to the slide by means of adhesive. The whole was then placed in a desiccator and the pressure was reduced to about 50 mm. of mercury. With the aid of a funnel and tap, Bakelite cement grade NPA was poured into the ring. The whole was then removed from the desiccator and baked for 24 hr. at 85°–95° C. The stainless steel ring was removed and the mounted specimen was ground on emery papers starting with Durex grade 340 and finishing with grade 600. It was next ground with abrasive powders BM. 302 and 303½ (α alumina, Corundum), from the

British American Optical Co., Ltd., on lead foil backed by a flat glass plate. The specimens were then washed and polished on a Selvyt cloth wheel with diamond dust of 0-1 μ particle size. In all the above stages, paraffin was used as a lubricant. After washing, the specimen was given a final polishing on a Selvyt pad with a water paste of fine alumina made by firing hydrated aluminium sulphate at about 900° C. This preparation makes it possible to distinguish between cupric and cuprous oxide in the scale, since the former is appreciably darker than the latter. To show up grain boundaries, specimens were etched for 3-10 sec. in 5% solution of sodium or potassium cyanide. The cupric oxide was not appreciably attacked.

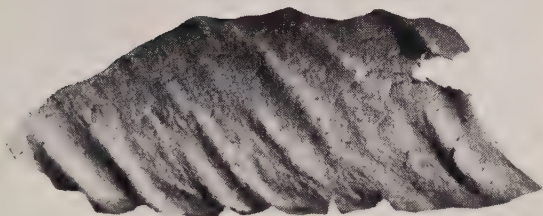
Figs. 9 and 10 (Plate XXXVIII) show a section through adherent scale on tough-pitch copper (NPE) formed by oxidation at 900° C. for 1 hr. and cooled in air. A small amount of cupric oxide is revealed by etching (Fig. 10). The dark areas indicate porosity.

Figs. 11 and 12 (Plate XXXIX) show a section of exfoliated scale from deoxidized copper (NPF) produced by oxidation at 900° C. for 1 hr. but removed by twisting at 800° C. The porosity of this scale is very much greater than that on the tough-pitch copper, and the grain-size a good deal smaller. However, the small grain-size is not due to phosphorus alone, since the other copper containing phosphorus (NTF) after oxidation for 1 hr. at 900° C. and air-cooling had a scale of large grain-size (see Fig. 13, Plate XL). It appears that in the scales from phosphorus-containing coppers there is a layer of small grain-size near the metal/oxide interface. This layer seems to be completely detached from the bulk of the scale, which has a larger grain-size (Fig. 14, Plate XL); it is believed, however, that, before mounting, it must have been connected to the body of the scale at some points at least. Examination of the small-grain-size zone showed some signs of intergranular separation, and it appeared possible that there might be a grain-boundary constituent causing a form of hot tearing under the stress caused by differential contraction.

In an attempt to produce more of this possible intergranular constituent, a copper containing 0.25% of phosphorus was oxidized at 900° C. for 16 hr. The field shown in Fig. 15 (Plate XLI) was taken from the centre of the scale produced by this treatment. A constituent is clearly visible at the junction of some of the grains, and it forms stringers along most of the boundaries. Fig. 16 (Plate XLI) shows this constituent at higher magnification. Here the light areas have a definite copper colour.

In order to identify the constituent, pieces of copper-phosphorus alloy of composition Cu_3P (approximating to 15% phosphorus) were

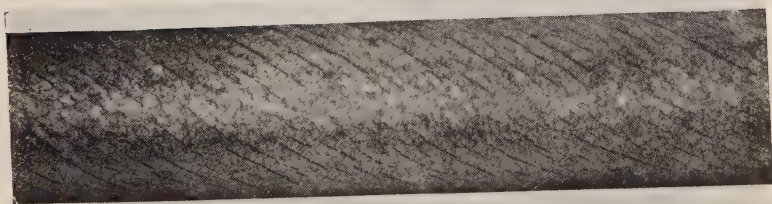
←—Axis of Rotation.—→



(a)



(b)



(c)

FIG. 4.—Methods of Scale Failure.

- (a) Compressive buckling of brittle scale formed at 900° C. and twisted at 800° C. on copper + 0.03% phosphorus (NTF). $\times 3.5$.
- (b) Hot tearing between buckles in a scale formed at 900° C. on copper + 0.03% phosphorus. $\times 3.0$.
- (c) Tensile cracking of brittle scale at 400° C. (twisted in opposite direction to (a) and (b)). $\times 3.0$.



FIG. 5.—Section of Oxide Wire from "Pure" Copper (NTB).
× 115.



FIG. 6.—As Fig. 5, etched in sodium cyanide. Approx. × 100.

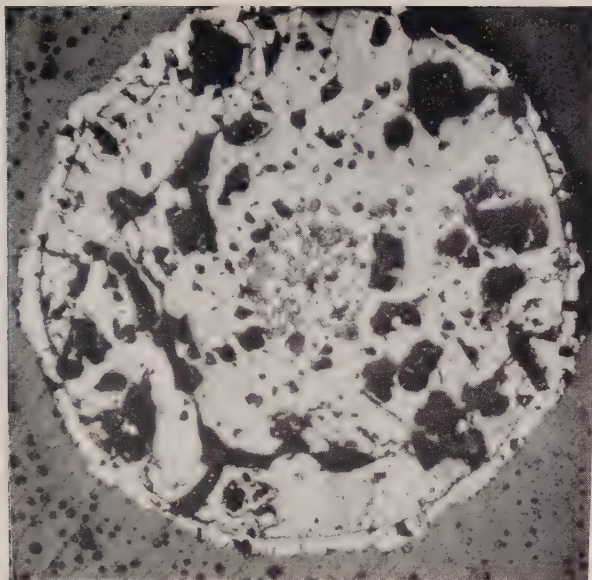


FIG. 7.—Etched Section of Oxide Wire from Copper + 0.03% Phosphorus (NTF). Approx. $\times 100$.

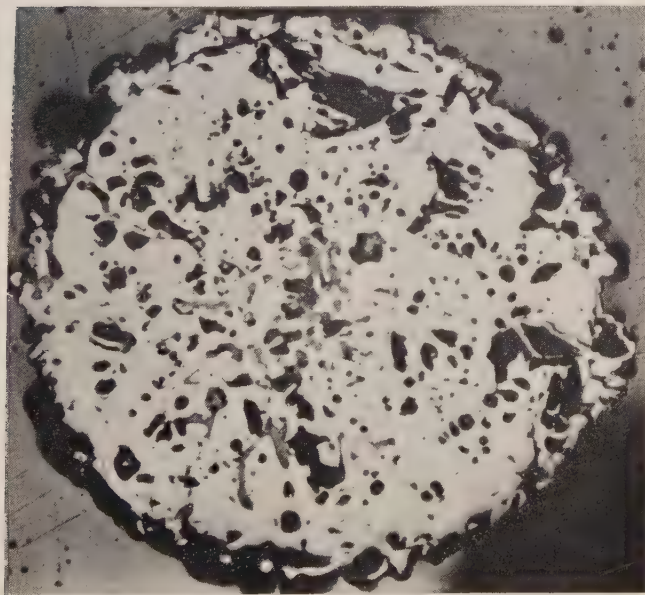


FIG. 8.—Section of Oxide Wire from Arsenical Copper (OCA). Approx. $\times 100$.



FIG. 9.—Section through Scale on Tough-Pitch Copper (NPE)
Oxidized at 900° C. for 1 hr. Unetched. $\times 300$.

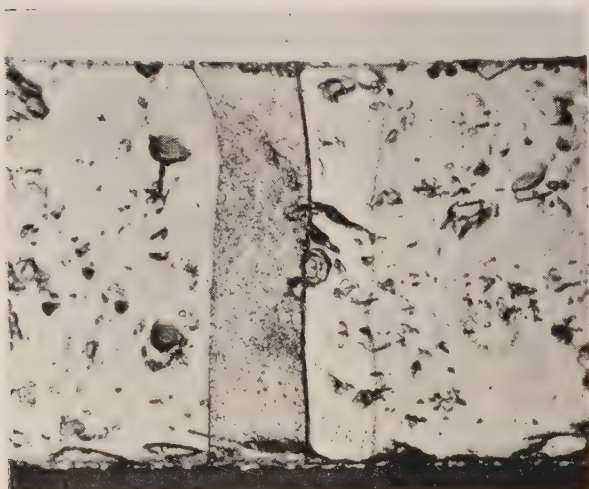


FIG. 10.—As Fig. 9. Etched. $\times 300$.



FIG. 11.—Exfoliated Scale from Deoxidized Copper (NPF)
Oxidized at 900° C. for 1 hr. and Twisted at 800° C. Unetched.
× 100.

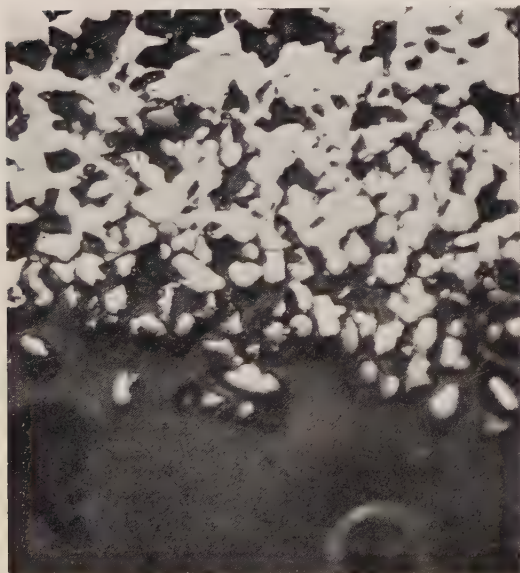


FIG. 12.—As Fig. 11. Fine-Grained Area near Scale/Metal
Interface. × 500.

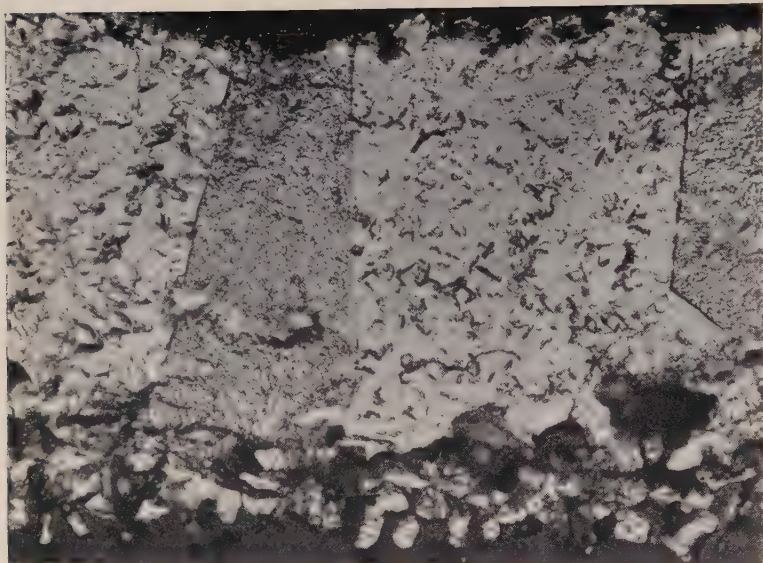


FIG. 13.—Scale Exfoliated from Copper + 0.03% Phosphorus (NTF) Oxidized at 900° C. for 1 hr. $\times 450$.

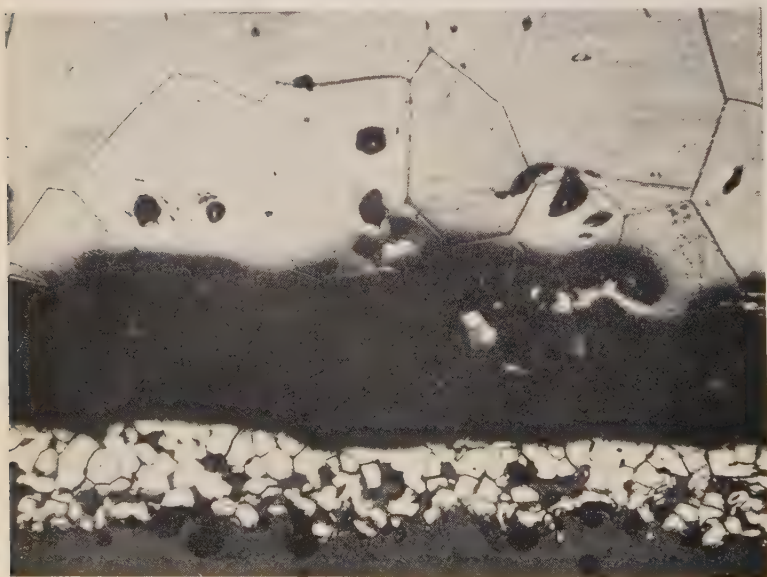


FIG. 14.—Scale Exfoliated from Copper + 0.03% Phosphorus (NTF) Oxidized at 800° C. for 4 hr. $\times 300$.

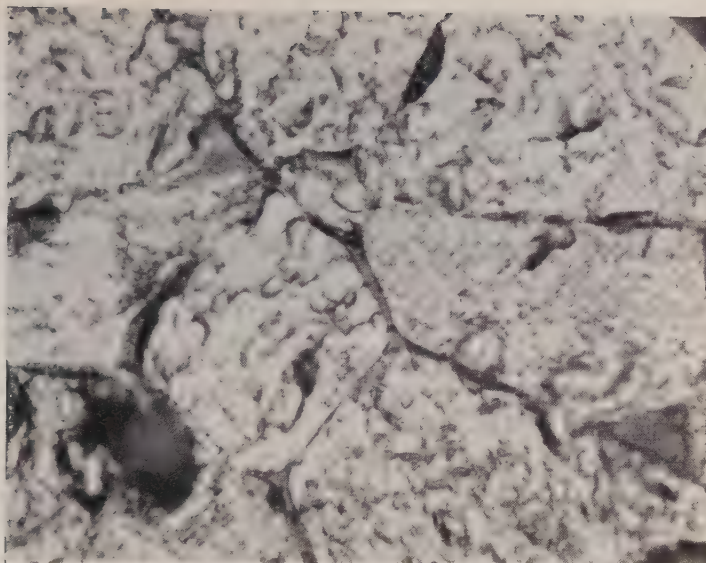


FIG. 15.—Centre of Scale from Copper + 0.25% Phosphorus (DOG) Oxidized at 900° C. for 16 hr. $\times 500$.



FIG. 16.—Intergranular Constituent from Oxide Shown in Fig. 15. $\times 2000$.

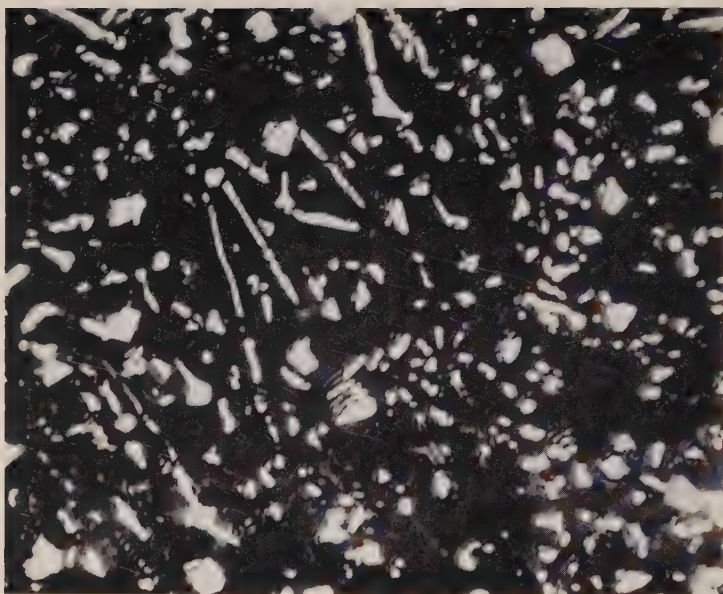


FIG. 17.—Slag Liquated from Copper + 15% Phosphorus Alloy Oxidized at 680° C. $\times 1000$.

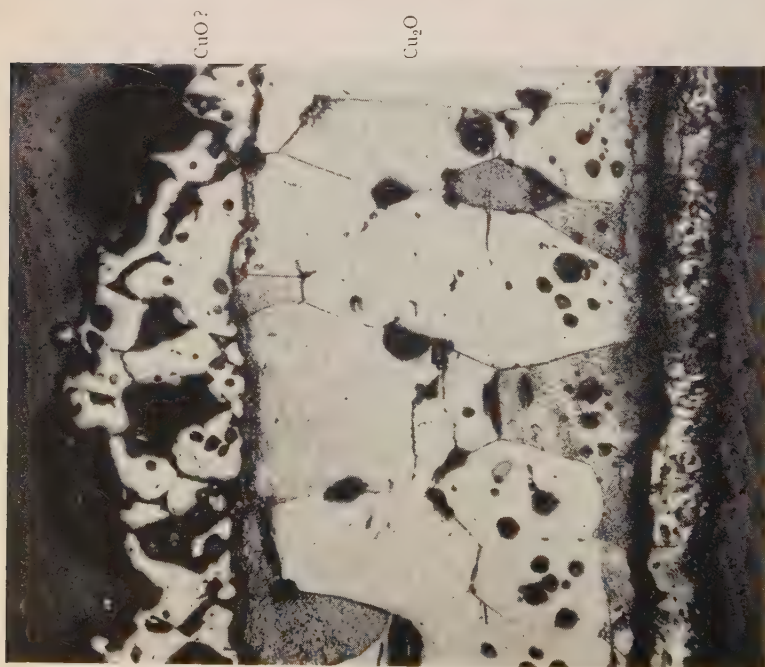
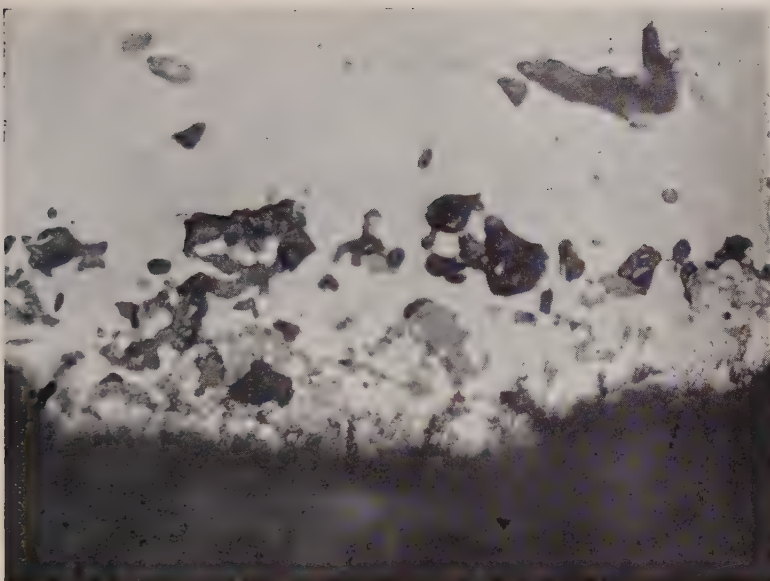


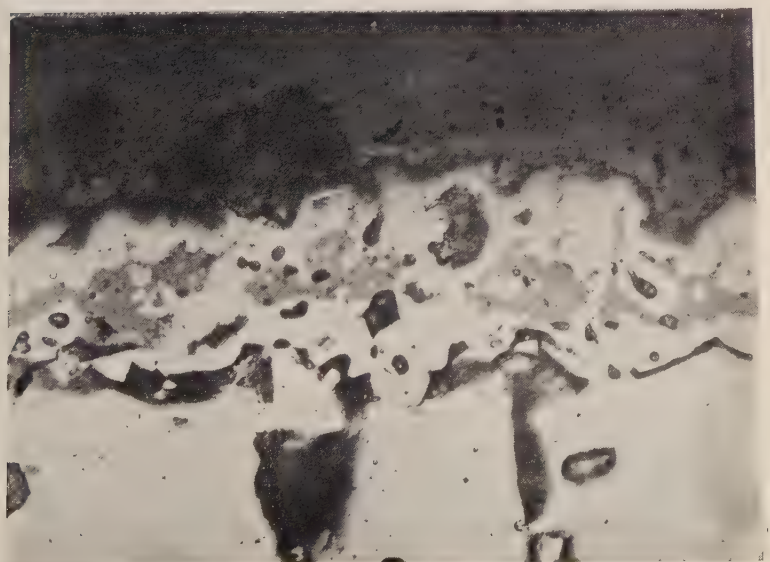
FIG. 18.—Scale Exfoliated from Tough-Pitch Arsenical Copper (OCB) Oxidized at 900° C. for 4 hr. Approx. $\times 200$.



Cu_2O

Cu_2O
+ ?

FIG. 19.—Scale from Tough-Pitch Arsenical Copper Showing Second Phase in Cu_2O Layer near Metal/Scale Interface. $\times 400$.



CuO
+ ?

Cu_2O

FIG. 20.—Scale from Tough-Pitch Arsenical Copper Showing Second Phase in CuO Layer. $\times 400$.



FIG. 21.—Slag from Oxidation of Copper + 30% Arsenic Alloy Oxidized at 650° C. $\times 200$.

oxidized at 680° C., i.e. below the melting point of the copper-phosphorus eutectic. The oxidation product was a fluid slag which ran to the bottom of the crucible and could be poured off from the solid pieces of copper-phosphorus alloy. On cooling, it became progressively more viscous and appeared to become solid at about 500° C. A piece of this slag was sectioned and polished with the result shown in Fig. 17 (Plate XLII). The light areas again exhibit a coppery colour. From the similarity in the appearance of the intergranular constituent and the slag produced by the above method, it appeared reasonable to assume that the compositions were similar. Chemical analysis of the slag gave its composition as copper 65.1, phosphorus 11.5, oxygen 23.3%. This corresponds approximately to the formula $(\text{Cu}_2\text{O})_n\text{P}_2\text{O}_5$, where $n = 2.8$, suggesting that the oxidation product is substantially cuprous phosphate Cu_3PO_4 . If it is assumed that the copper-coloured second phase in the slag is metallic copper, and its volume as deduced from Fig. 17 is subtracted from the total copper content, it is found that the composition of the remainder corresponds to the formula $\text{Cu}_3(\text{PO}_4)_2$. It is thus fairly definitely established that the intergranular constituent is cuprous phosphate, which on cooling breaks down into free copper and cupric phosphate.

Photomicrographs of scales from arsenical copper (Figs. 18-20, Plates XLII and XLIII) showed the presence of large quantities of another phase, both in the layer near the metal/oxide interface (Fig. 19) and at the interface between the cupric oxide and cuprous oxide layers near the surface of the scale (Fig. 20). There was very much less in the centre of the scale, although it was apparent in the microsection of the corresponding oxide wire (Fig. 8, Plate XXXVII).

A small amount of copper-arsenic alloy containing 30% arsenic (approximate composition of Cu_3As) was made by melting the correct proportion of copper and arsenic in a sealed system. The two metals were sealed in an evacuated silica tube, and the whole was heated for an hour at 1100° C. The Cu_3As so prepared was oxidized at 650° C., i.e. below the melting point of the copper-arsenic eutectic. The oxidation product was a viscous slag which was slowly decomposed to give off white arsenious oxide. On cooling, the slag was found to be grey, brittle, and extremely porous. A section was made, and showed a two-phase structure upon examination (Fig. 21, Plate XLIV). The dark areas are pores, presumably due to the evolution of arsenious oxide while hot, and the white areas are possibly unoxidized alloy. The bulk of the slag consists of the grey constituent which closely resembles the third phase in scales from arsenical copper. The composition of the slag was copper 73.3, arsenic 17.8, oxygen (by difference) 8.9%. This

composition has a deficiency of arsenic compared with the starting material, in agreement with the observed volatilization of arsenious oxide. It is not possible to assign a definite formula to the grey phase.

VII.—DISCUSSION.

The results presented enable a fairly clear picture to be obtained of the behaviour of the scales on phosphorus-containing and phosphorus-free coppers, especially as regards the behaviour of scales formed at about 900° C. The behaviour of scales on arsenical copper is less easy to understand.

For the first two types of copper it appears that exfoliation of the scale during cooling is largely the result of stresses produced by differential thermal contraction, which imposes a difference in strain between copper and scale of about 0.16% (0.0016) for each 100° C. change in temperature. In the present experiments, in which the copper itself is well supported and cannot easily deform, it is reasonable to assume that this strain is practically all taken up in the scale, which is thus submitted to a two-dimensional compression of the magnitude stated.

The variations in the behaviour of different scales during cooling are therefore presumably due to the differences in the strain which they can accommodate, and the results reported show that the behaviour can in fact be correlated with the amount of deformation which the scale-metal systems can tolerate in shear at different temperatures. In spite of the different method of deformation, the strains to failure in shear (hot-torsion tests) are of the same order as the strains to failure calculated from the results of the exfoliation tests. Thus the minimum fall in temperature before the start of exfoliation is 70° C., corresponding to a two-dimensional compression of 0.001, and the minimum shear strain to failure in the hot-torsion test is 0.003. Although there are instances where the results of the two types of test do not roughly correspond, for instance in the case of the scales formed at 700° C., these are comparatively few and appear to represent borderline cases in which the properties are changing rapidly with temperature.

No scale has been observed to exfoliate in cooling at a temperature in excess of 530° C. and this fact is in agreement with the observation from the torsion test that all scales will withstand moderate deformation at temperatures above 600°–700° C. There is nevertheless a large difference between the coppers with and without phosphorus at temperatures from 600° C. upwards, the latter being much more deformable at these temperatures.

There are reasons to suppose that these differences are caused by

differences in the bulk properties of the scales. Support for this view is obtained from comparison of torsion-test results on scales formed on tough-pitch copper at 900° C. in 1 hr. and in 4 hr.; although the film is twice as thick in the second case and any interfacial stresses are therefore likely to be doubled, the results are substantially the same. (Table VIII). Further confirmation is received from the results of the tensile tests on wires of oxide formed at 900° C.; the oxide formed from copper containing phosphorus was very much less ductile than the other when tested in the range 600°–900° C.

TABLE VIII.—*Effect of Oxidation Time at 900° C. on Shear Strain to Failure of Tough-Pitch Copper (NPE).*

Twisting Temperature, ° C.	Oxidation Time	
	1 hr.	4 hr.
900	>0.7	>1.0
800	>0.7	>1.0
700	>0.8	>0.87
600	0.55	>0.87
500	0.26	0.24
400	0.055	0.035

The cause of the loss of ductility of scales formed at 900° C. in the presence of phosphorus is clearly shown by the metallographic work. Copper with 0.25% phosphorus forms a scale containing substantial quantities of a phase which is shown to be cuprous phosphate, and on cooling this phase breaks down to cupric phosphate and copper. The phosphate is liquid at the temperature of formation, and becomes progressively more viscous on cooling, like a glass. Examination of the photomicrograph (Fig. 15, Plate XLI) indicates that on many of the boundaries the “dihedral angle” is very low. It has been shown by C. S. Smith³ that with such low angles the grain-boundary phase will spread to cover a large part of the grain-boundary area, even if present in very small quantity, so that quite a small amount of phosphorus would be expected to cause embrittlement of the scale.

The scales on arsenical tough-pitch copper are intermediate in behaviour between those on the coppers without phosphorus or arsenic and those on phosphorus-containing coppers. Their behaviour, however, is apparently somewhat inconsistent, both in itself and with the picture outlined above. Those formed at the highest temperatures exfoliate on cooling, as do the scales on coppers containing phosphorus, but at somewhat lower temperatures. Those formed at lower temperatures also exfoliate, but less readily than either of the other two types.

In the torsion test the properties are on the whole similar to those of scales on coppers free from phosphorus and arsenic. Thus the scales formed at 600° C. and below have slightly superior ductility in this test to their counterparts on the other coppers, in agreement with the exfoliation-test results, and those formed at the highest temperatures in 1 hr. also have properties in the range 600° C. and below which are superior to those of scales on pure or tough-pitch copper, in spite of the fact that they exfoliate on cooling. The apparent discrepancy can be explained, however, by assuming that the temperature at which the scales become brittle is below the lowest torsion-test temperature (400° C.). This is consistent with the low temperature at which exfoliation occurs (<200° C.). There are still anomalies, however, since, although the torsion-test figures for the range 400°–900° C. for scales formed at 900° C. largely follow those for pure copper scales, the tensile test on wires yields results much more like those for scales containing phosphorus. Moreover, there is disagreement between torsion-test results on 900° C. scales formed in 1 hr. and 4 hr., respectively when tested at low temperatures (Table VIII). The explanation may lie in the volatility of arsenious oxide from the scales and in the apparently uneven distribution of the embrittling constituent in these scales. Alternatively, the large proportion of the low-melting-point phase in some parts of the scales (see Figs. 19 and 20, Plate XLIII) may have permitted movement of the mixture of solid and liquid under shear and compressive stresses, whereas the same material would have little capacity for deformation in tension. It is clear, however, that much more work would be required to obtain a true understanding of the behaviour of arsenical scales.

In view of the great ductility shown by scales formed on pure and tough-pitch coppers at 900° C. when tested in the temperature range 600°–900° C., e.g. elongations at failure in tension of 10–25% and shear strains at failure in the torsion test of 0.5 and over, it is somewhat surprising at first sight that such scales are commonly removed during hot working. The explanation appears to lie in the chilling effect of the rolls. When the hot billet, at for instance 900° C., is brought into contact with the rolls, which might be at 50° C., an extremely steep temperature gradient is set up in the surface layers of the rolls and in the scale. The outside of the scale is thus initially chilled to quite a low temperature and would be likely to crack from the deformation produced in rolling. In the Appendix (p. 323) is given a discussion of the thermal conditions and estimates of the temperatures reached by the inside and outside of the scale at various times. The results are shown in Fig. 23.

It will be seen that the temperature of a point at the outside of the

scale is 255°C. at the moment of contact, rising, in the case of a scale formed in 4 hr. at 900°C. , to 435°C. in 0.25 sec. (a typical time of contact during rolling). The inside of the same scale falls from 900° to 760°C. in about 0.25 sec. These figures must be regarded as approximate, since not only is the treatment not exact but the thermal constants used in obtaining the actual values are not in all cases well established. In particular, the conductivity of cuprous oxide may be a good deal higher at these temperatures than the value used, which was obtained at $25^{\circ}\text{--}30^{\circ}\text{C.}$ The use of a higher value would lead

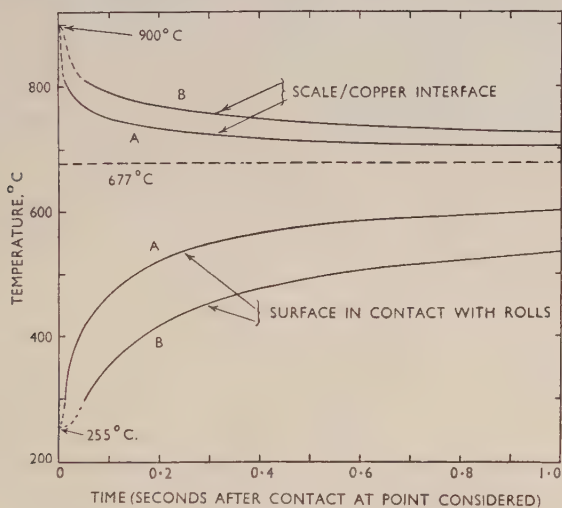


FIG. 23.—Temperature of Scale during Rolling.

Curves A : Rolled after 1 hr. at 900°C.

" B : " 4 " "

to a higher initial temperature at the outside of the scale. The results show clearly, however, that the temperature of the outer surface is at the start below the ductile range, so that cracking is likely to be initiated which may spread throughout the scale. Moreover, at the end of the period of contact the temperatures in the scale cover the transition range from brittle to ductile scales, and a small variation of conditions, conductivities, or scale composition might make a large difference to whether the scale was removed in hot rolling or not. For instance, if the billet temperature on entering the rolls is below 900°C. , as it will be in subsequent passes or with a lower preheating temperature, the temperatures produced in the scales will be correspondingly lower.

VIII.—CONCLUSIONS.

(1) Scales formed on high-purity oxygen-free and tough-pitch coppers at temperatures from 400°–600° C. are substantially non-adherent, but at temperatures above 700° C. they are strongly adherent and will withstand a large amount of deformation while sufficiently hot.

(2) Scales on coppers containing phosphorus are also non-adherent when formed at temperatures up to 600° C. Those formed at higher temperatures withstand somewhat more deformation without failure while hot, but become sufficiently brittle on cooling to exfoliate readily.

(3) The strain, imposed by differential contraction of oxide and metal, required to start exfoliation of the most brittle scales on cylindrical specimens is about 0.001 corresponding to a fall in temperature of about 70° C. In a torsion test, in which the scales are submitted to shear, the most brittle scales are caused to fail by a shear strain of the order of 0.003 (i.e. of the same order of magnitude).

(4) The properties of scales formed at 900° C. on coppers with and without phosphorus have been investigated in some detail. The adherence judged by the temperature of exfoliation on cooling or the extent of exfoliation when cold, can be correlated with the properties as revealed in the torsion test. Thus, although the scale on phosphorus-free metal is much more ductile, both kinds of scale will withstand moderate shear strains (in excess of about 0.02) at 600° C. and above. At 500° C. and below, the scale on phosphorus-containing copper has very little ductility, and hence the strains imposed by thermal contraction on cooling substantially below this temperature cause exfoliation. The scales on coppers without phosphorus, on the other hand, retain substantial ductility down to 400° C. (the lowest temperature of test); these scales do not exfoliate.

(5) For these coppers the behaviour in the torsion test can be correlated with the bulk properties of the scale, as measured in a tensile test on a specimen consisting entirely of scale. For pure copper the extension at fracture was from 3% at 500° C. to 25% at 900° C. and for phosphorus-containing copper it varied from 1% at 400° C. to 3% at 900° C. and the maximum value was 5%.

(6) This difference in behaviour is accounted for by a grain-boundary constituent which has been observed in scales from coppers containing 0.25% phosphorus and for which there is some evidence in the coppers of lower phosphorus content. This constituent is formed as cuprous phosphate and decomposes on cooling to cupric phosphate and copper. At the temperature of formation it is liquid, and it cools to a glass. It appears to form stringers in most of the grain boundaries, and should

therefore act as an embrittling agent, even if present in very small quantity.

(7) The scales on arsenical copper are intermediate in behaviour between those on the coppers without phosphorus or arsenic and those on coppers with phosphorus. Their behaviour, however, is apparently somewhat inconsistent, both in itself and with the picture outlined above, and it is clear that further work would be required to gain a full understanding of their properties. Those formed at high temperature (900°C.) have a glassy constituent similar to that of the phosphorus scales, which would be expected to cause the exfoliation on cooling which is observed.

(8) In hot rolling, the scale is initially chilled at the outer surface to a temperature at which even the most ductile type will withstand little deformation. At the end of the period of contact, the temperatures in the scale are in the range of transition from brittle to ductile properties, so that the conditions determining whether a crack in the surface of the scale will be propagated are probably rather critical.

ACKNOWLEDGEMENTS.

The author is indebted to the Director and Council of the British Non-Ferrous Metals Research Association for permission to publish this paper. He also wishes to acknowledge the helpful advice received from Mr. W. A. Baker and Mr. R. Eborall and to thank the latter for his valuable Appendix to this paper.

APPENDIX.

THE TEMPERATURE OF THE OXIDE SCALE ON COPPER DURING HOT ROLLING.

By R. EBORALL, M.A., MEMBER.

In the hot-rolling process a slab initially of moderately uniform high temperature passes through rolls which are initially comparatively cold. Any single point on the surface of the slab is suddenly brought into contact with the cold roll surface and remains in contact with it for a period determined by the roll speed and the reduction in thickness during the pass. In what follows, it is assumed that the speed of approach of this chosen point to the rolls is such that cooling of the point by conduction along the length of the slab, before the moment of contact, is negligible, and that the conditions at any one point at the interface, after contact, approximate to those existing when a scaled copper surface initially at a uniform temperature T_B is suddenly placed in good contact with a steel block initially at a uniform temperature T_R . Thus it is implicit that the main flow of heat, during the short period

of contact, is normal to the interface, and that the flow parallel to the surface is negligible. The deformation of the copper is also neglected; this deformation will have the effect of bringing hot copper towards the interface, and so will cause the actual scale temperatures to rise somewhat towards the exit end of the arc of contact compared with the calculated values.

1. *The Outer Surface of the Scale (Scale/Roll Interface).*

At the instant of contact and for a short time afterwards the distances, normal to the surface, over which temperature changes take place, are small relative to the thickness of the oxide layer. The oxide can then be considered as extending to infinity in one direction and the steel of the rolls in the other. These conditions represent a well-known problem,⁴ and the surface temperature T_S is given by :

$$T_S = T_R + (T_B - T_R) \frac{K_F \alpha_F^{-\frac{1}{2}}}{K_F \alpha_F^{-\frac{1}{2}} + K_R \alpha_R^{-\frac{1}{2}}} \quad . \quad . \quad (1)$$

where K = thermal conductivity, α = thermal diffusivity ("temperature diffusivity"), and the suffixes F , R , and B denote film (cuprous oxide), rolls (steel), and billet (copper), respectively.

For steel ⁵ :

$K = 0.115 \text{ cal. cm.}^{-1} \text{ sec.}^{-1} \text{ }^\circ\text{C.}^{-1}$ (for 1% carbon steel at 18° C.)

Specific heat = $c = 0.1045 \text{ cal. }^\circ\text{C.}^{-1} \text{ g.}^{-1}$ (at 0° C.)

Density = $\rho = 7.87 \text{ g./c.c.,}$

so that $\alpha = \frac{K}{c\rho} = 0.140 \text{ cm.}^2/\text{sec.}$

For copper ⁵ :

$K = 0.918 \text{ cal. cm.}^{-1} \text{ sec.}^{-1} \text{ }^\circ\text{C.}^{-1}$ (at 18° C.)

$c = 0.0909 \text{ cal. }^\circ\text{C.}^{-1} \text{ g.}^{-1}$ (at 0° C.)

$\rho = 8.93 \text{ g./c.c.,}$

and so $\alpha = 1.13 \text{ cm.}^2/\text{sec.}$

For cuprous oxide ^{6, 7} :

$K = 0.0146 \text{ cal. cm.}^{-1} \text{ sec.}^{-1} \text{ }^\circ\text{C.}^{-1}$ (at 25°–30° C.)

$c = 0.460 \text{ joules. }^\circ\text{C.}^{-1} \text{ g.}^{-1}$ (at 0° C.)

$= 0.110 \text{ cal. }^\circ\text{C.}^{-1} \text{ g.}^{-1}.$

$\rho = 6.0 \text{ g./c.c.,}$

and so $\alpha = 0.0221 \text{ cm.}^2/\text{sec.}$

We thus have :

$$\left. \begin{array}{l} K_R = 0.115, K_B = 0.918, K_F = 0.0146 \\ \alpha_R = 0.140, \alpha_B = 1.13, \alpha_F = 0.0221 \end{array} \right\} \text{C.G.S. units.}$$

These values are for temperatures about room temperature and would perhaps be somewhat different at the operating temperatures, but are thought good enough for this approximate treatment.

From these values :

$$T_S = T_R + (T_B - T_R) \times 0.241 \quad . \quad . \quad (1A)$$

Inserting, as typical values :

$$\text{Roll temperature} = T_R = 50^\circ \text{ C.}$$

$$\text{Billet temperature} = T_B = 900^\circ \text{ C.}$$

$$T_S = (50 + 850 \times 0.241)^\circ \text{ C.} \\ = 255^\circ \text{ C.}$$

This solution breaks down after a short time, such that the temperature at the oxide/copper interface starts to change significantly, i.e. after about 10^{-3} sec. for the film formed in 1 hr. at 900° C. , and the surface temperature of the oxide then starts to rise. The period of contact is actually much longer than this. Taking as typical a roll surface speed of 2 ft./sec., and a roll dia. of 2 ft. 6 in., for a reduction in one pass of 2 in. (1 in. on each roll), i.e. 40% on a 5 in. thick billet, the period of contact is 0.23 sec.

For times much longer than 10^{-3} sec. (from about 0.01 sec. upwards under the conditions considered) a good approximation is given by considering the oxide film merely as an obstruction to heat flow, and neglecting the variation in the heat stored in it.* The solution is again known⁴ and is :

$$T_S = T_R + (T_B - T_R) \frac{K_B \alpha_B^{-\frac{1}{2}}}{K_B \alpha_B^{-\frac{1}{2}} + K_R \alpha_R^{-\frac{1}{2}}} \{1 - e^{y^2} (1 - \text{erf } y)\} \quad (2)$$

$$\text{where } \text{erf } y = \frac{2}{\sqrt{\pi}} \int_0^y e^{-y^2} dy,$$

$$y = \sqrt{t} \cdot \frac{K_F}{x} \cdot \frac{K_B \alpha_B^{-\frac{1}{2}} + K_R \alpha_R^{-\frac{1}{2}}}{K_B \alpha_B^{-\frac{1}{2}} \cdot K_R \alpha_R^{-\frac{1}{2}}}$$

and x = thickness of oxide film.

If the numerical values of the diffusivities and conductivities are inserted, we have :

$$y = \frac{\sqrt{t}}{x} \times 0.0644$$

$$\text{and } T_S = T_R + (T_B - T_R) 0.738 \{1 - e^{y^2} (1 - \text{erf } y)\} \quad . \quad (2A)$$

* At still longer times the temperature at the centre of the billet begins to fall, and this fall has an effect on the conditions at the scaled surface. The effect, however, is not significant for times of contact less than about 1 sec. for a 2 in.-thick slab and longer for larger slabs, and so can be neglected.

where x is in cm., and t is in sec. (See ref.⁴ for table of $e^{y^2}(1 - \operatorname{erf} y)$). The term in curly brackets is equal to 0 when $t = 0$, giving $T_S = T_R$, and tends asymptotically to 1 as t becomes large.

At 900° C. in air, the weight of oxygen absorbed by copper is about 9.3 mg./cm.² after 1 hr., or 18.6 mg./cm.² after 4 hr. (Tylecote²), corresponding to thicknesses of 1.38×10^{-2} cm. and 2.76×10^{-2} cm. respectively. T_S has been calculated as a function of t for both these values, and with the same initial roll and billet temperature (50° C. and 900° C.). The resulting curves are shown in Fig. 23.

2. The Inner Surface of the Oxide Film (Scale/Copper Interface).

The temperature of the copper/copper oxide interface (T_{FB}) is initially that of the billet, in this case 900° C. After about 10^{-3} sec. (for the film formed in 1 hr. at 900° C.) the temperature starts to fall and after about 0.01 sec. it approximates closely to :

$$T_{FB} = T_R + (T_B - T_R) \frac{K_B \alpha_B^{-\frac{1}{2}}}{K_B \alpha_B^{-\frac{1}{2}} + K_R \alpha_R^{-\frac{1}{2}}} \left\{ 1 + \frac{K_R \alpha_R^{-\frac{1}{2}}}{K_B \alpha_B^{-\frac{1}{2}}} \cdot e^{y^2} (1 - \operatorname{erf} y) \right\} \quad (3)$$

where $y = \sqrt{t} \cdot \frac{K_F}{x} \cdot \frac{K_B \alpha_B^{-\frac{1}{2}} + K_R \alpha_R^{-\frac{1}{2}}}{K_B \alpha_B^{-\frac{1}{2}} \cdot K_R \alpha_R^{-\frac{1}{2}}}$, as before.

With numerical values for diffusivity and conductivity, this becomes :

$$T_{FB} = T_R + (T_B - T_R) \times 0.738 \{1 + 0.356 e^{y^2} (1 - \operatorname{erf} y)\},$$

and
$$y = \frac{\sqrt{t}}{x} \times 0.0644 \quad . \quad . \quad . \quad . \quad (3A)$$

The times of contact for which this equation is valid are the same as for equation (2).

The resulting curves for the oxide films formed after 1 hr. and 4 hr. preheating at 900° C. are again given in Fig. 23.

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THE OXIDATION OF COPPER AT 350°–900° C. 1282

IN AIR.*

By R. F. TYLECOTE,† M.A., M.Sc., A.I.M., MEMBER.

(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

As part of a study of the adherence of oxide scales on copper and on phosphorus-deoxidized copper, the oxidation rates of these materials in air were measured in the temperature range 350°–900° C., by a continuous-weighing method. At 615° C. and higher the coppers oxidize according to the parabolic law, and the rate constants are similar for the two types. At lower temperatures the initial stages of oxidation depart significantly from the parabolic mode and the oxidation probably follows a logarithmic law, the rates again being similar for the two types of copper. However, as the scale thickens, the oxidation conforms more nearly to the parabolic law. At about 450°–500° C. there is a change of slope in the plot of the parabolic rate constant against the reciprocal of the absolute temperature, and at this temperature there is a similar change of slope in the analogous plot of the electrical conductivity of the oxide film. The second change is thought to account for the first and, if this is correct, no alteration in the mechanism of parabolic oxidation need be postulated. The results of the work have no direct bearing on the adherence of the scales on the two types of copper except in so far as the adherence may depend in part on the thickness of the scale.

I.—INTRODUCTION.

A SURVEY of literature ¹ on the oxidation and scaling of copper and its alloys showed that only limited information was available on the nature and rate of growth of oxide films in the temperature range 400°–700° C., and that little was known of the characteristics determining the adherence of films and scales formed at these and higher temperatures. A separate paper ² describes experiments on the properties of oxide scales on various coppers and an account is now given of experiments on the oxidation rate of certain coppers in dry air. The information available on the oxidation rates of copper suggested that there might be a change in the mechanism of oxidation at about 600°–700° C., and it was thought that a fuller understanding of the mechanism in the temperature range involved in the working of copper and its alloys, namely 350°–900° C., was likely to assist in understanding the scaling behaviour of the materials, this being the primary object of the research. Accordingly, the oxidation rates of several coppers have been measured over this

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temperature range, with a view to establishing the oxidation laws obeyed at various temperatures and thus throwing more light on the mechanism involved.

II.—MATERIALS.

Two batches of specially refined copper were vacuum-melted and cast, each with and without a small phosphorus addition. The main difference between the two batches lay in the silver content, which it was thought might influence the scaling characteristics. A high-purity tough-pitch copper (CCC brand) was also available, and a part of this was remelted in a Salamander crucible in a gas-fired furnace, deoxidized with phosphorus, and cast in air. These materials were all rolled and drawn to 5/16 in. dia. rod. The last draw was preceded by a pickle and was made without lubricant. The compositions of the materials are given in Table I of the earlier paper.²

III.—EXPERIMENTAL TECHNIQUE.

1. *Method of Weighing.*

An analytical balance was adapted for continuous weighing of a specimen during oxidation, as used by White³ and others.⁴ In this method the specimen is suspended freely in the furnace from a wire attached to one end of the balance beam, and weight measurements are made at intervals while the specimen is at temperature. In the present experiments the specimen was heated in nitrogen, and air was admitted when the temperature was steady, usually after 15 min. These gases were purified, as described below. The zero for the time scale was taken as the moment when air was admitted to the furnace. This continuous-weighing method avoids difficulties due to exfoliation of the scale during cooling, and to changes in the weight of the scale after cooling.

The balance was one of the aperiodic projection type, reading up to 200 mg. on the illuminated scale to a sensitivity of 0.1 mg. A platinum wire about 18 in. long was fixed to a hook mounted between the two verticals of the left-hand pan frame. It passed through a hole in the pan and through the hole in the case normally occupied by the pan support, and the specimen, attached to its lower end, hung freely in the centre of a vertical tube furnace.

The furnace tube was of silica, 1½ in. (3.2 cm.) bore, and had two metal flanges cemented to it, on to which were fixed plates, carrying at the lower end the gas inlet and thermocouple tubes, and at the upper end the gas outlet. The bottom of the furnace tube was packed, to just below the specimen, with crumpled Brightray wire in order to improve heat transfer to the moving gas. The outlet tube was

of glass and was T'd half-way along its length. The vertical limb of the T extended upwards into the balance case and the suspension wire passed through it, while the branch tube was connected to an extraction apparatus. Sufficient suction was applied to this branch to extract from the furnace the hot gases which would otherwise enter the balance case. Some of the air in the balance case was also withdrawn, so that it was necessary for the balance to be used in a room with reasonably constant temperature. The effect of the heat from the furnace on the temperature of the balance was minimized by interposing an insulating screen.

The zero of the instrument was checked at intervals during the test by bringing the beam to rest, transferring the specimen-suspension to a fixed hook provided nearby, replacing by a mass equivalent to the initial weight of the specimen, and freeing the beam again. A check was made while the specimen was heating-up in nitrogen just before the air was admitted and at intervals during the oxidation. Corrections were made to individual readings when necessary according to the zero drift. It is considered that the individual weight readings at the lower temperatures (350°–615° C.) are accurate to ± 0.022 mg./cm.². (See Appendix B, p. 348).

The temperature was measured by a thermocouple inserted into the furnace tube from the bottom end. The bare end of the thermocouple was $\frac{1}{4}$ in. above the lower end of the specimen and midway between the specimen and the wall of the furnace tube. The difference between the temperature indicated by the thermocouple and that of the specimen was determined at each temperature in a separate experiment, but the differences were negligible.

2. Specimens and Atmosphere.

On arrival the material was stored in desiccated containers until required, i.e. for periods up to six months. Immediately before use the rods, 0.79 cm. in dia., were cut into specimens 7 cm. long. For the initial tests at 615° C. and above, the specimens were degreased in acetone. A second test at 615° C., with a specimen pickled for 15 sec. in 10% sulphuric acid at 60° C. and then washed in water and dried with acetone, gave results which were slightly, but scarcely significantly, higher. Accordingly, in the more critical tests at lower temperature the specimens were pickled in the same way to remove the tarnish film formed during storage.

The nitrogen in which the specimens were heated to the temperature of the experiment was purified by passing it through alkaline pyrogallol, and dried, finally, with phosphorus pentoxide. The air for oxidation

was drawn from a cylinder and purified by passing it over solid potassium hydroxide, magnesium perchlorate, and phosphorus pentoxide. Slight oxidation frequently occurred during heating-up in nitrogen to temperatures above about 600° C., but this was never equivalent to more than 1 min. of oxidation in air at the same temperature.

3. Buoyancy Corrections.

The weight of nitrogen or air displaced by the specimen varies with the temperature, and there is consequently an apparent increase in weight during heating-up as shown in Table I.

TABLE I.—*Data for Buoyancy Corrections.*

Temperature, ° C.	Apparent Increase in Weight in Nitrogen, mg./cm. ² equivalent of the weight change. (Specimen area 18.4 cm. ²)
20	0
400	0.12
500	0.13
600	0.15
700	0.16
800	0.16
900	0.17

There is a further small change in weight on substituting air for nitrogen at the temperature of the experiment. This was about 0.05 mg. (0.003 mg./cm.²) at 400° C. and less at higher temperatures.

For oxidation at 615° C. and above, the weight-increases plotted in the oxidation/time curves were obtained by reference to the weight of the cold specimens, after allowing for the change in weight due to the buoyancy effect. Below 615° C., where more accurate readings were required, the method was found to be unreliable owing to erratic drift in the zero of the balance before the admission of air, and the weight-increase was obtained by reference to the apparent weight of the specimen at the time of admission of air.

IV.—RESULTS.

During the progress of the work it became clear that at high temperatures the oxidation of copper appeared to behave strictly according to the parabolic law :

$$w^2 = Kt \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where w is the weight increase per unit area, t the time, and K a constant, in agreement with the results of Pilling and Bedworth.⁵

At low temperatures, however, there were departures from this

relationship. The results are therefore presented in two sections dealing with: (1) the temperature range 615°–908° C. in which the parabolic law appears to be almost exclusively obeyed, and (2) the range 350°–550° C. in which it has been found that a more complex relationship exists in the early stages of oxidation.

1. Oxidation Between 908° and 615° C.

In Figs. 1–3 the square of the weight of oxygen absorbed per unit area is plotted against the time. Straight lines are obtained in every



FIG. 1.—Oxidation in Dry Air at 908° and 806° C. (square of weight increase against oxidation time).

KEY.

- Copper (NPV).
- × Copper + 0.03% phosphorus (NPW).
- + Tough-pitch copper (NPE).

case but one, confirming that the parabolic law is obeyed, except for one phosphorus-containing copper at 615° C. (Fig. 3, NTF). The results are summarized in Table II, from which it can be seen that the values of the rate constant (K) are of the same order for the six coppers examined.

2. Oxidation Between 550° and 350° C.

As already mentioned, preliminary experiments showed that there was a departure from the parabolic type of oxidation at low temperatures.

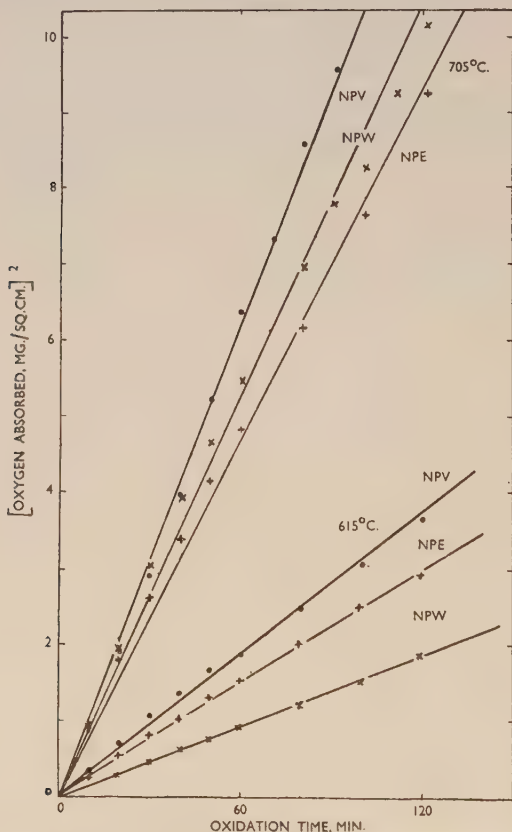


FIG. 2.—Oxidation in Dry Air at 705° and 615° C. (square of weight increase against oxidation time).

KEY.

- Copper (NPV).
 × Copper + 0.03% phosphorus (NPW).
 + Tough-pitch copper (NPE).

The oxidation of two specially refined coppers with and without phosphorus (NTF and NTB-C-E) was therefore investigated and the times of oxidation were increased, e.g. to 10 hr. at 550° C. and to 170 hr. at 350° C. The results obtained at five temperatures in the range 550–350° C. are presented in Figs. 4–8. In these figures the values of

TABLE II.—*Parabolic Oxidation Rates of Coppers Between 908° and 615° C.*

Temperature, ° C.	Specially Refined (Oxygen-free)				Specially Refined with Phosphorus				Commercial Copper (CCC. Brand)			
	NTB (0.0005% Ag)		NPV (0.001% Ag)		NTP (0.0005% Ag)		NPW (0.001% Ag)		NPE (Tough-pitch)		NPF (Phosphorus Deoxidized)	
	Wt. Increase, mg./cm. ² after 1 hr.	K , g. ² cm. ⁻⁴ hr. ⁻¹	Wt. Increase, mg./cm. ² after 1 hr.	K , g. ² cm. ⁻⁴ hr. ⁻¹	Wt. Increase, mg./cm. ² after 1 hr.	K , g. ² cm. ⁻⁴ hr. ⁻¹	Wt. Increase, mg./cm. ² after 1 hr.	K , g. ² cm. ⁻⁴ hr. ⁻¹	Wt. Increase, mg./cm. ² after 1 hr.	K , g. ² cm. ⁻⁴ hr. ⁻¹	Wt. Increase, mg./cm. ² after 1 hr.	K , g. ² cm. ⁻⁴ hr. ⁻¹
908	9.30	8.7×10^{-5}	9.40	8.8×10^{-5}	9.90	9.8×10^{-5}	9.20	8.7×10^{-5}	9.20	8.5×10^{-5}	9.60	9.1×10^{-5}
806	4.70	2.2×10^{-5}	4.70	2.2×10^{-5}	4.10	1.7×10^{-5}	4.40	1.9×10^{-5}	4.80	2.3×10^{-5}	4.90	2.4×10^{-5}
705	2.20	4.8×10^{-6}	2.50	6.3×10^{-6}	2.30	5.3×10^{-6}	2.40	5.8×10^{-6}	2.30	4.9×10^{-6}	2.40	5.7×10^{-6}
615	1.00	1.0×10^{-6}	1.30	1.7×10^{-6}	0.97	9.4×10^{-7}	0.97	9.4×10^{-7}	1.20	1.4×10^{-6}	0.96	9.3×10^{-7}

 K = Parabolic rate constant. (Calculated from oxygen absorbed after 1 hr.)

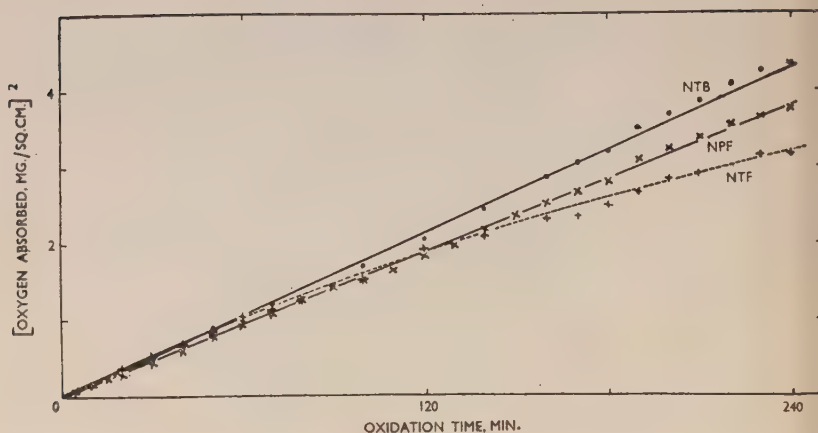


FIG. 3.—Oxidation in Dry Air at 615° C. (square of weight increase against oxidation time).

KEY.
 ● Copper (NTB).
 + Copper + 0.3% phosphorus (NTF).
 × Deoxidized copper (NPF).

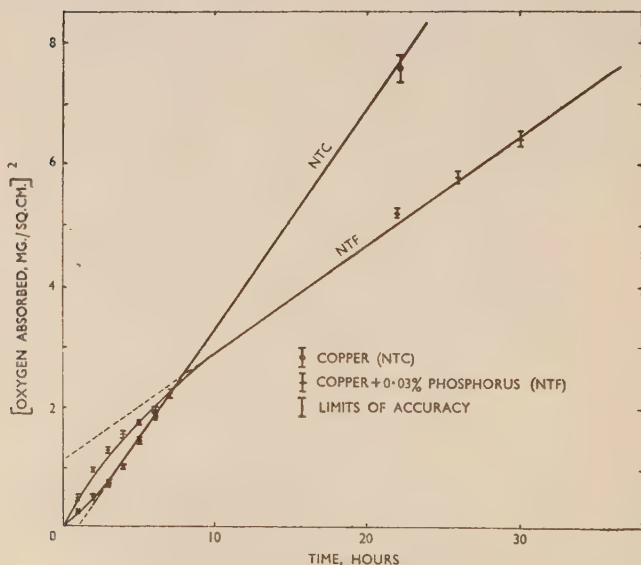


FIG. 4.—Oxidation in Dry Air at 550° C. (square of weight increase against oxidation time).

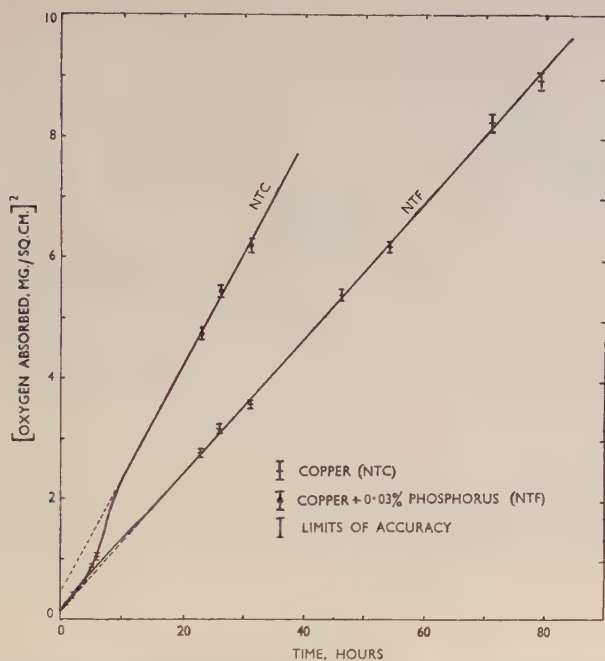


FIG. 5.—Oxidation in Dry Air at 510° C. (square of weight increase against oxidation time).

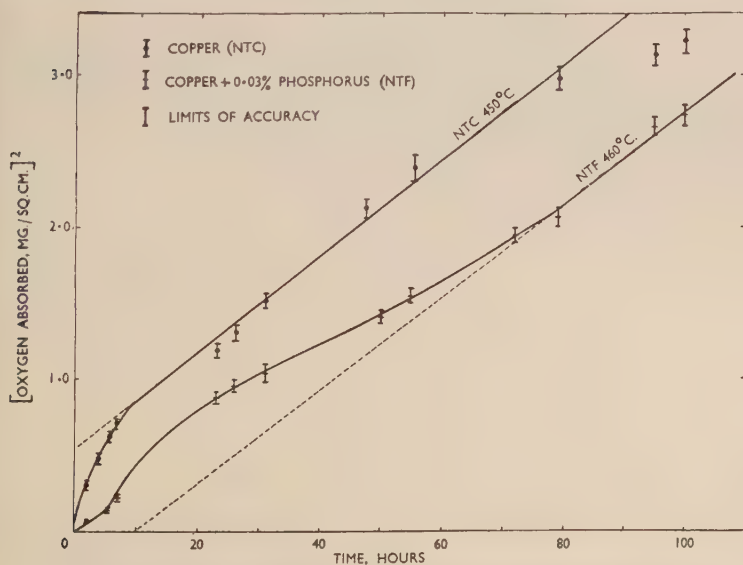


FIG. 6.—Oxidation in Dry Air at 450°–460° C. (square of weight increase against oxidation time).

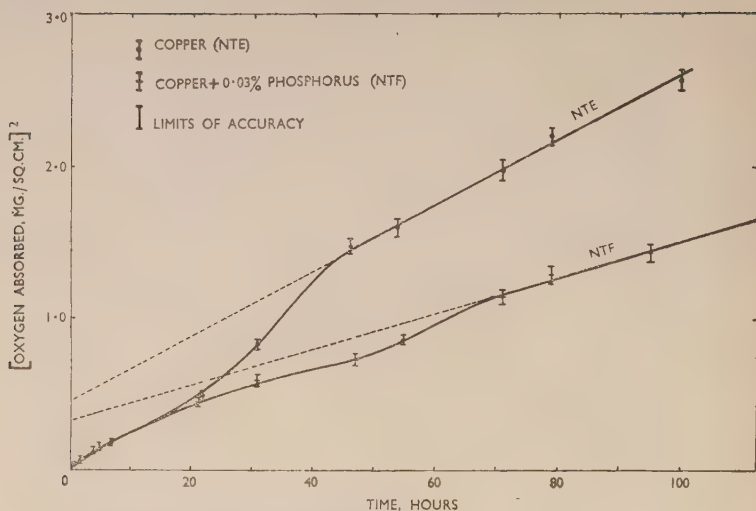


FIG. 7.—Oxidation in Dry Air at 405° C. (square of weight increase against oxidation time).

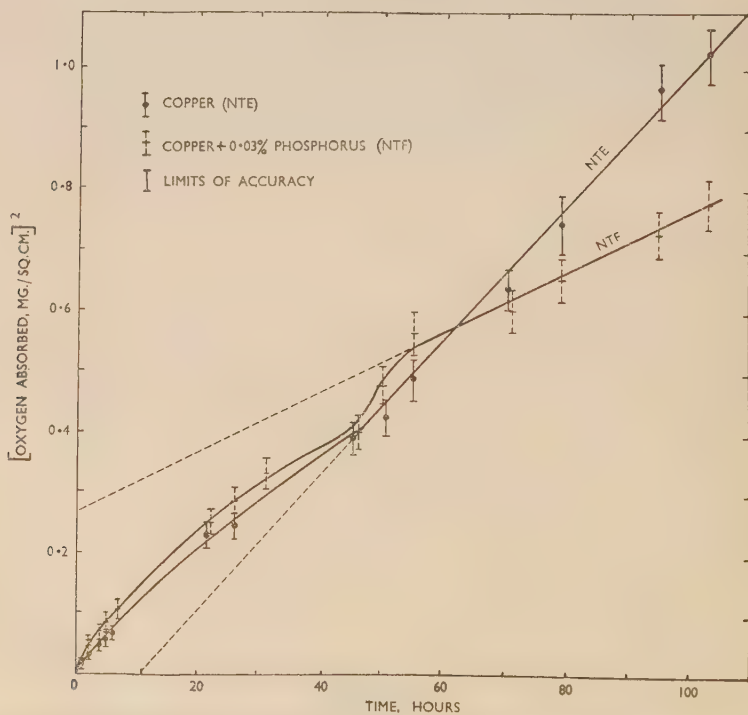


FIG. 8.—Oxidation in Dry Air at 350° C. (square of weight against oxidation time).

the square of the weight-increases per unit area are shown as vertical lines which indicate the ranges of experimental error involved in the weighings. It can be seen that for the weight-increases towards the end of each experiment straight lines can be drawn through the plotted ranges for a limited number of points, but that these lines extrapolated back to shorter times do not pass through the origin, as would be required by oxidation according to equation (1). It may be concluded that the oxidation does not conform throughout with the parabolic law, although the results are not incompatible with a parabolic oxidation law of the type $w^2 = Kt + C$ in the later stages of the tests.

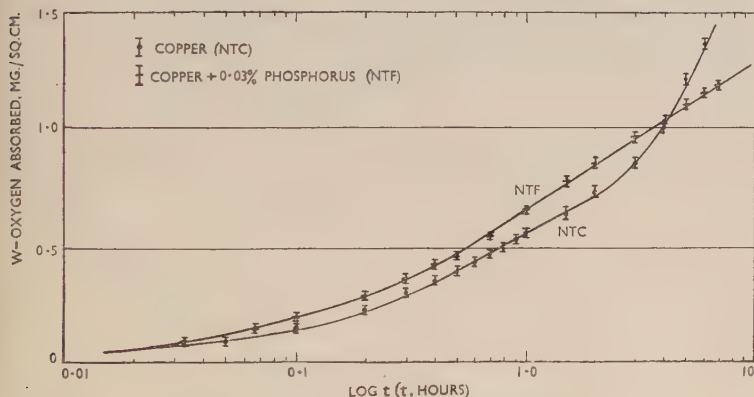


FIG. 9.—Oxidation in Dry Air at 550° C.

In Figs. 9 and 10 the weight-increases for oxidation at 550° and 350° C. are plotted against the logarithms of the times, and it can be seen that the results fall on straight lines for large parts of the oxidation periods, suggesting conformity with a logarithmic law.

Whatever the oxidation law, if it is assumed that the properties of the oxide film are characteristic of the weight w , and that the only effect of temperature is to accelerate a single process of oxidation, then for a normal activated process :

$$w = f(te^{Q/RT}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and hence, for constant w :

$$t = \text{constant} \times e^{Q/RT}$$

or

$$\log_e t = \text{constant} + \frac{Q}{RT}$$

where T = abs. temperature, R = gas constant, Q = the "activation" energy (a constant), and t = time.

It follows that the logarithmic plots of the oxidation curves for each material should coincide exactly, if each curve is transposed along the $\log t$ axis by an amount determined by Q and the value of T for each curve. In fact, the curves for each material could not all be made to coincide in this way. These observations suggest that, in both materials, either more than one process is occurring and that these processes have different activation energies, or alternatively that the assumption that the films formed at different temperatures have similar properties when of equal thickness, is in general wrong.

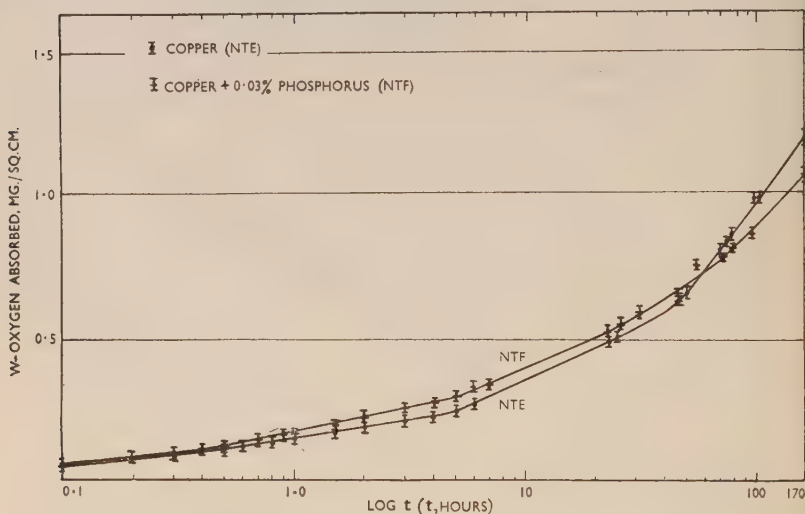


FIG. 10.—Oxidation in Dry Air at 350° C.

During the middle stages of oxidation in these experiments the $w/\log t$ plots can be approximated by straight lines for all experiments. This suggests adherence to a logarithmic oxidation law of the type observed for zinc at low temperatures,⁶ for which :

$$w = W \log_e \left(\frac{t}{t_0} + 1 \right) \quad . \quad . \quad . \quad (3)$$

where W and t_0 are constants, having the dimensions of weight per unit area and of time respectively. When w is plotted against $\log t$ for times large compared with t_0 , this relation approaches a straight line cutting the $\log t$ axis at $\log t_0$; for shorter times it gives a curve similar to those obtained experimentally.

As a check on the validity of the logarithmic equation, the weight

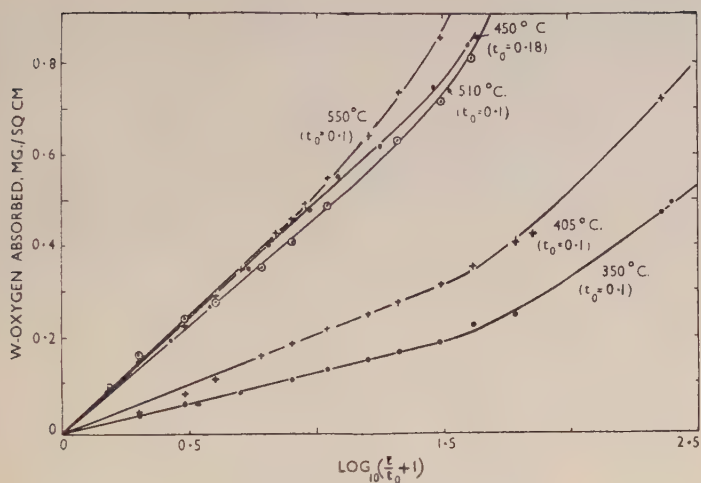


FIG. 11.—Oxidation of Copper (NTE).

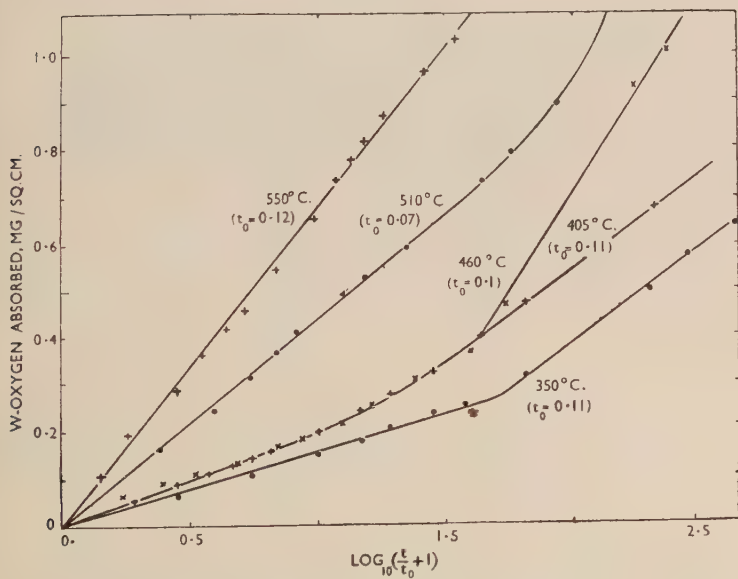


FIG. 12.—Oxidation of Copper + 0.03% Phosphorus (NTF).

increase may be plotted against $\log_{10} \left(\frac{t}{t_0} + 1 \right)$ using values of t_0 obtained as above. If the oxidation follows equation (3), a straight line through the origin, of slope $2.303 W (= W \log_e 10)$ should be obtained. Figs. 11 and 12 show such plots for pure copper and copper containing phosphorus, respectively. It will be seen that for pure copper the equation fits the results, within experimental error, from zero time onwards for a large part of the oxidation time. For copper containing phosphorus a good fit is obtained during the equivalent period at 550° and 510° C., but it appears possible that there may be two logarithmic stages, with different values of W and t_0 , at 460° C. and below.

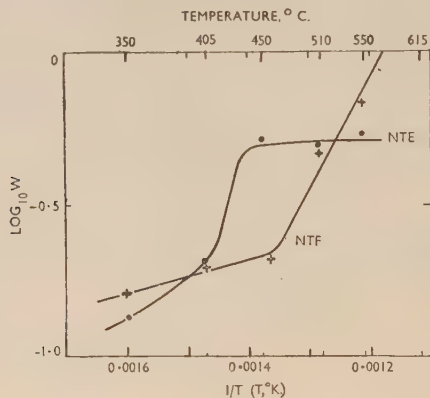


FIG. 13.—Effect of Temperature on Constant W .

The ranges of weight-increases over which the logarithmic relationship is valid (excluding any second logarithmic stage for the copper containing phosphorus) and the values of the constants W and t_0 are summarized in Tables III and IV. The figures for the range of validity are necessarily somewhat approximate. Those for t_0 are accurate only to about $\pm 15\%$. $\log W$ is plotted against $\frac{1}{T}$ in Fig. 13.

If curves of the type given by equation (3) have equal values of W , then the rate of growth at any particular thickness and the time taken to reach any thickness are both determined solely by t_0 , being proportional to $1/t_0$ and to t_0 , respectively. This is the behaviour expected if the properties of the film at any given temperature are characteristic of the film thickness and independent of the temperature of formation. $1/t_0$ is then a true rate constant and might be expected to vary with temperature in the usual way. In fact, however, W is dependent on

the temperature (Fig. 13), but t_0 varies from experiment to experiment and its variation with temperature is not very marked (Table III). The same kind of behaviour has been noted for zinc ⁶ and for copper at low temperatures.⁷

TABLE III.—*Constants for Logarithmic Portions of Oxidation Curves of Specially Refined Copper (NTB-C-E).*

Oxidation Temperature, ° C.	Range of Validity, mg./cm. ²	Time Constant t_0 , hr.	W , mg./cm. ²
550	0–0.82	Parabolic oxidation only 0.1	0.532
510	0–0.71 0–0.57	0.1 0.06	0.478 0.450
450	0–0.109 0–0.114	0.18 0.16	0.510 0.528
405	0–0.44 0–0.33	0.10 0.16	0.212 0.190
350	0–0.22	0.10	0.131

TABLE IV.—*Constants for Logarithmic Portions of Oxidation Curves of Specially Refined Copper containing Phosphorus (NTF).*

Oxidation Temperature, ° C.	Range of Validity, mg./cm. ²	Time Constant t_0 , hr.	W , mg./cm. ²
550	0–1.30 0–1.14	0.11 0.12	0.683 0.683
510	0–0.81 0–0.52	0.07 0.07	0.440 0.430
460	0–0.38 * 0–0.27 *	0.13 0.10	0.201 0.212
405	0–0.35 * 0–0.35 *	0.07 0.11	0.200 0.196
350	0–0.27 *	0.11	0.158

* Applies only to range represented in this table. There are probably other logarithmic portions to these curves.

The results presented show that at 550° C. and below, the early stages of oxidation are in accordance with a logarithmic relationship, while at longer times it appears possible that a parabolic oxidation law is obeyed, but the exact point of transition from one law to another is

difficult to determine. This is further complicated by the fact that in some cases the logarithmic curve appears to be in two portions.

Assuming that the oxidation in the present experiments did in fact obey the parabolic law in the last stages of the tests at 550° C. and below,

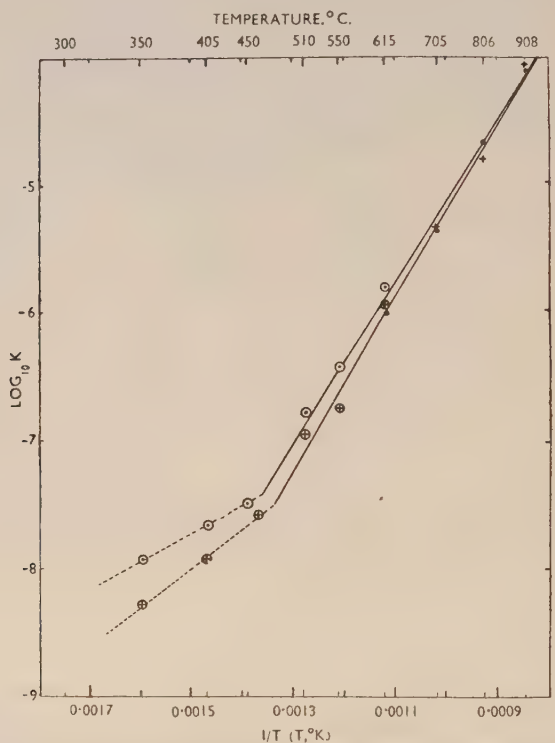


FIG. 14.—Temperature Dependence of the Parabolic Rate Constant.

KEY.

Copper (NTB, NTC, NTE)	{ ● as drawn.
	{ ○ pickled.
Copper + 0.03% phosphorus (NTF)	{ + as drawn.
	{ ⊕ pickled.

the values of the rate constant K have been determined from the slopes of the straight lines in Figs. 4–8. These values are plotted in Fig. 14 together with the values obtained from the tests at higher temperatures. From this graph of $\log K$ against the reciprocal of the absolute temperature, it is seen that the points fall close to a single straight line down to between 450° and 500° C. At lower temperatures the points for the two coppers fall on two lines of smaller slope. This change in slope occurs at a lower temperature than has hitherto been obtained, the

majority of results by other workers on various coppers having tended to a change in slope at about 600° C.

V.—DISCUSSION.

The experiments of Pilling and Bedworth⁵ showed that from 700° C. upwards, in air or oxygen, tough-pitch copper oxidized according to a parabolic relation, the square of the weight-increase being proportional to the time of oxidation. Between 700° and 400° C. their lowest test temperature, experiments were carried out in oxygen only, and considerable scatter in results was obtained. They found that the rate of oxidation was always equal to or above that expected from an extrapolation of the high-temperature results, and they attributed the deviations to cracking of the oxide film. At lower temperatures, early workers using individual weight determinations^{8,9} again found the parabolic law to hold, but recent workers are in general agreement that it does not do so at all exactly, although the conclusions of different investigators about the oxidation laws actually obeyed are somewhat at variance. Thus Lustman and Mehl,⁷ who dealt with the oxidation of single crystals of oxygen-free high-conductivity copper in air at temperatures from 80° to 155° C., concluded that for each experiment, after the first 1 or 2 min., there were one or more linear relations between the thickness of the film and the logarithm of the time of oxidation. Dighton and Miley¹⁰, working on tough-pitch copper at 180°–288° C., interpreted their results in terms of an initial parabolic stage followed by a logarithmic stage. Campbell and Thomas,¹¹ who studied the oxidation of oxygen-free high-conductivity copper between 100° and 256° C., considered their results to approximate best to an equation of the type $w^3 = Kt + C$, where w is the weight-increase in time t , and K and C are constants. A feature common to all these results is that the rate of reaction slows up with the growth of the film to a more marked extent than it does for the parabolic growth law.

In the intermediate temperature range the only results appear to be those of Hudson and his co-workers¹² on tough-pitch arsenical copper at temperature from 260° to 600° C. On the basis of individual weight determinations at 1, 2, 4, and 6 hr. at 400° C., they concluded that oxidation was parabolic.

At temperatures of 700° C. and above, the present results agree with those of Pilling and Bedworth,⁵ and there is little or no difference between the different coppers. The change in the form of oxidation curve expected from the above published work is found to occur at about 500° C. The results obtained between 350° and 550° C. hardly support the cracking hypothesis of Pilling and Bedworth, since the

oxidation curves are smooth within the limits of experimental error. The conformity of the results with the logarithmic equation :

$$w = W \log_e \left(\frac{t}{t_0} + 1 \right) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in the early stages of oxidation, is in general agreement with the results of other workers ^{7, 10} at lower temperatures. A difficulty here is that this form of equation can be made, by a suitable choice of the two constants, to conform to a rather wide range of curves, and that to provide a rigorous test of the equation a very high experimental accuracy would be required.

The mode of transition from the low-temperature to the high-temperature oxidation mechanism in pure copper seems of interest. It appears likely that at any particular temperature the low-temperature mechanism persists to a certain film thickness, at which the parabolic mechanism becomes operative. The thicknesses at which the change takes place (0.2 — 1.1 mg./cm.² or about 10⁵ Å.) are of the same order as the "barrier layer" in copper/copper-oxide rectifiers ¹³ as determined by measurements of electrical capacity; this correspondence appears to support the contention of Campbell and Thomas ¹¹ that the departure from the parabolic relationship at low temperatures is a consequence of the peculiar electrical conditions in these thin films, rather than that the logarithmic relation is due to the growth of the oxide as discrete islands ¹⁴ or to the gradual closing up of flaw paths in the oxide.¹² The existence of cavity-barriers distributed at random is another mechanism, suggested by Evans,¹⁵ which could lead to the logarithmic growth law. In very thin films, cavity-barriers (blisters) would not be expected owing to the ability of the film to withstand compressive stresses without breakdown. Such films on copper would thicken parabolically. However, as the film thickness increased, blisters would be formed which would slow down the rate of growth, and probably give rise to the logarithmic law. It would be necessary to put forward an explanation to account for the transition from the logarithmic to the parabolic law at a constant temperature. This could probably be explained on the basis of Evans's theory, by a tendency to form vertical cracks or flaw paths, rather than blisters, as the film thickens. Investigation of the properties of the films would probably be required to settle this point. The conditions at these temperatures are in any case somewhat complicated by the existence of a substantial outer layer of cupric oxide.

The parabolic rate constants vary with temperature in the manner expressed by the Arrhenius equation :

$$K = Ae^{-Q/RT} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Where A is a constant ($\text{g.}^2 \text{ cm.}^{-4} \text{ hr.}^{-1}$), R is the gas constant, T the abs. temperature, and Q the activation energy (cal.).

A plot of the logarithm of the rate constants against the reciprocals of the absolute temperature is given in Fig. 14. It will be seen that over the temperature range 900°–500° C., the points fall reasonably near to a straight line. At lower temperatures the few points available are represented by a second straight line of lower slope. On the basis of Hoar and Price's electrochemical interpretation of Wagner's theory of parabolic oxidation,¹⁶ such a change in slope would occur if there were a change in slope in the analogous plot for electrical conductivity, such as was found by Zhuze and Kurchatov.¹⁷ The measurements reported in Appendix A, show that for a wire of oxide formed by oxidation at 900° C. such a break occurs at about 500° C., in agreement with the oxidation results.

The values of constant A , and the activation energy Q , obtained from the straight lines in Fig. 14 are shown in Table V.

TABLE V.—*Values of A and Q Obtained from Fig. 14.*

Material	Temperature Range, ° C.	A , $\text{g.}^2 \text{ cm.}^{-4} \text{ hr.}^{-1}$	Q , cal.
"Pure" Copper (NTB, NTC, NTE) Cu + 0.04% Phosphorus (NTF)	900–600	40	29,400
	900–600	50	31,600
"Pure" Copper (NTB, NTC, NTE) Cu + 0.04% Phosphorus (NTF)	500–300	1.8×10^{-5}	9,300
	500–300	3.2×10^{-3}	13,700

Not too much importance should be attached to the figures for the lower range of temperature, since these are based on three points only.

If these constants are compared with those given in an earlier paper,¹ it will be seen that the values obtained by previous workers are somewhat diverse and dependent upon temperature. Q varies from 29,000 to 42,000 cal. in the temperature range 500°–1030° C. As mentioned there, it appears that the values actually conform to a curve, a view expressed by Valensi.¹⁸ The two straight lines normally obtained by plotting the logarithm of the rate constant against the reciprocal of the absolute temperature are thought by Valensi to be the extreme tangents to a curve.¹⁸

Another reason for the increase in activation energy with temperature may be the presence of small amounts of impurities in the coppers used by many previous workers. It is possible that some of these impurities appear in the scales in the form of compounds with oxygen and copper.

This seems to be the case with phosphorus and arsenic, and a marked increase in the oxidation rate of a 0.4% arsenical copper was observed at 900° C.² This may be the reason for the slightly higher activation energy obtained with the phosphorus-containing copper shown above.

In the lower temperature range, below 900° C., the present author's values of activation energy are much lower than those obtained by other workers. If these values are correct, the discrepancy may be due to the fact that other workers have assumed parabolic oxidation throughout, and their values are based on observations made at relatively short times (1–6 hr.). During this period, according to the results now given, oxidation is not parabolic. The author's constants are based only on the oxidation rates obtained when the parabolic stage of oxidation is reached, i.e. after periods varying from 10 hr. at 500° C., to 100 hr. at 350° C.

VI.—CONCLUSIONS.

It is felt that the results reported warrant the following conclusions, although it is recognized that those relating to oxidation in the temperature range 350°–550° C. are necessarily tentative owing to the limited accuracy of the methods used :

(1) Oxidation of all coppers investigated follows the parabolic law down to about 615° C. This observation does not preclude the rate law being different during the first minute or so of oxidation.

(2) At temperatures between 550° and 350° C. oxidation of copper, with or without phosphorus, may originally be logarithmic but as the scale thickens the oxidation probably becomes parabolic. The thickness at which the apparent transition takes place is of the order of 10^5 Å. (0.7 mg./cm.²).

(3) The oxidation rates (K) obtained at high temperature are in agreement with those of Pilling and Bedworth.⁵ The rates vary with temperature in the normal way, i.e. a plot of $\log K$ against $1/T$ is a straight line. Below 450°–500° C. the rate constants for the (assumed) parabolic part of the oxidation curves lie above the straight line of $\log K$ against $1/T$ representing the results at high temperatures. However, no change in oxidation mechanism is indicated, because there is a corresponding change in the electrical conductivity of the oxide film.

(4) At temperatures from 600° to 900° C. all the coppers investigated had approximately the same oxidation rate at any given temperature. In other words, the amounts of phosphorus and oxygen present in de-oxidized and tough-pitch coppers have little or no effect on the oxidation rate. Below 600° C., however, the presence of phosphorus reduces the oxidation rate.

ACKNOWLEDGEMENTS.

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APPENDIX A.—*Effect of Electrical Resistance of Copper Oxide on Oxidation Rate.*

In the course of experiments on the mechanical properties of oxide wires reported elsewhere,² resistance measurements were made on the oxides of the coppers NTE and NTF while cooling from their formation temperature of 900° to 300° C. According to the electrochemical interpretation of Wagner's theory¹⁶ a metallic surface undergoing oxidation may be regarded as a current-producing cell with the metal/film and film/oxygen interfaces as anode and cathode, respectively. The film may be regarded as electrolyte and external circuit since it has both ionic and electronic conductivities. If this is so, the electrical conductivity of the oxide film will influence the rate of oxidation. The resistance measurements made on oxide wires afforded an opportunity to check the relationship.

The specimens of oxide were prepared by oxidizing wires 0.020 in. thick at 900° C. to completion. The end-point was determined by a resistance test. The oxidized wires were then slowly cooled in the furnace and resistance measurements were made during cooling. The method of preparation of the oxide film has some effect on the excess of oxygen over the stoichiometric composition and therefore influences the initial conductivity of the sample. This has been demonstrated in the work on conductivity of copper oxide by Zhuze and Kurchatov.¹⁷

The results of these experiments on the measurement of the conductivity of oxide wires are given in Fig. 15, in which the logarithm of the specific conductivity in ohms⁻¹. cm.⁻¹ is plotted against the reciprocal of absolute temperature. The result is a straight line over the range 900°–500° C., showing a pronounced departure beginning at temperatures of the order of 400°–500° C. This departure from linearity is in agreement with results obtained when the logarithm of the parabolic-oxidation rate constant is plotted against the reciprocal of absolute temperature (Fig. 14).

There can be no exact comparison between these results and the results of the oxidation tests, since the conductivity was measured longitudinally, whereas the current flow during oxidation is radial, and

in the conductivity tests the oxide was not in general formed at the temperature of measurement. Nevertheless, the similarity of the two sets of results strongly suggests that the departure from linearity at low temperatures in Fig. 14 does not indicate any fundamental difference in oxidation mechanism in the parabolic range but merely variations in rate of oxidation due to changes in electrical conductivity of the scale.

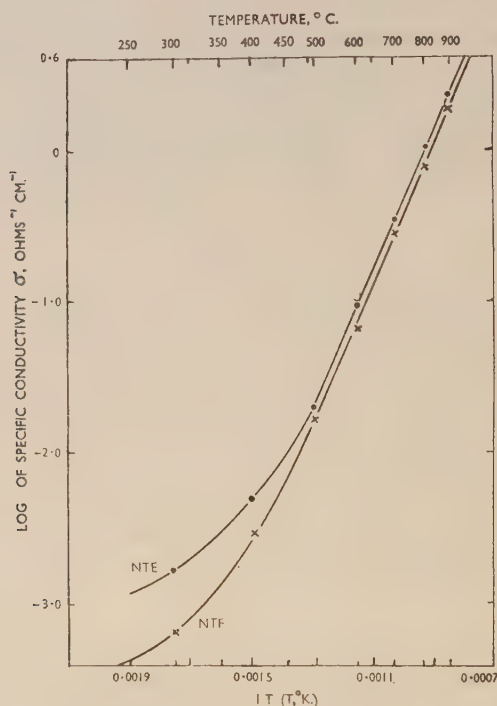


FIG. 15.—Variation of Conductivity of Oxide Wires with Temperature.

KEY.
 ● Copper (NTE). × Copper + 0.03% phosphorus (NTF).

APPENDIX B.—*Determination of Experimental Accuracy.*

In continuous-oxidation experiments, where the weight of the specimen being oxidized is measured by a balance of the projection type placed above the furnace in which the reaction is proceeding, it is extremely difficult to prevent the heat from the furnace affecting the accuracy of the balance. While the balance used in this work could be read to an accuracy of 0.1 mg. or better, the accuracy actually obtained

depended on the alteration of the zero of the balance between zero checks. The change of zero with time was not always linear and the estimation of zero at any given time was made difficult by the fact that the actual checking of the zero had a tendency to alter the zero reading of the balance. It was of course necessary to avoid putting the hands within the balance case, and the change from the oxidation specimen to the dummy specimen (which had the same initial mass as the oxidation specimen) was therefore made by means of a stiff wire which could be placed in a loop of the platinum suspension wire. By this means the oxidation specimen could be lifted from the hook on the balance arm. The dummy specimen was placed on the balance pan in the same way.

In the low-temperature oxidation range (350°–615° C.), where the zero drift tended to assume a greater proportional error than at high temperatures, estimates of the accuracy of the zero check were made by the following method. A number of runs were made in which the specimen was placed in the furnace under the usual conditions. Instead of the specimen being attached to the balance pan a mass equivalent to the initial weight of the specimen was left permanently in position. At intervals corresponding to the normal periods of zero checking this mass was temporarily removed and replaced, simulating the movements of the specimen, opening and closing balance doors, &c., which were normally carried out when checking the zero. It was found by this means that the maximum error that could be introduced by zero checking and changes in the zero between checks, was of the order ± 0.3 mg. Assuming a possible error in reading ± 0.1 mg., the total error possible becomes 0.4 mg. or 0.022 mg./cm.² on a specimen of surface area 18.4 cm.²

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INFLUENCE OF OXIDE ON THE PRESSING 1283 AND SINTERING OF COPPER COMPACTS.*

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SYNOPSIS.

The pressing and sintering of compacts of electrolytic copper powder have been studied with particular reference to the influence of oxide.

A single batch of powder was prepared, freed of oxide by hydrogen reduction at 255° C., and superficially oxidized to various oxygen contents ranging from 0.11 to 11.2 wt.-% by controlled low-temperature treatment in oxygen. Small cylindrical compacts were pressed at 10, 20, and 30 tons/in.²; their densities were determined in the green state and after sintering, and their length changes during controlled heat-treatments in reducing and neutral atmospheres were followed in detail dilatometrically.

The porosity of the green compacts, of the order of 15–40 vol.-%, decreases with increase of compacting pressure, and varies in a complex manner with oxygen content. The specific volume increases with increase of oxygen content, in a manner explained in terms of the specific volumes of solid copper and cuprous oxide and of their packing, deformation, and fragmentation during pressing.

During heat-treatment, the compact length at first increases: the length increase is greater than that due to solid thermal expansion, owing to the inflation produced by gas trapped in pores and (in reducing atmospheres) by gases produced in the reduction of oxide. The inflation increases with increase of initial oxygen content up to about 1–2 wt.-% and thereafter decreases. Shrinkage due to oxide reduction and/or metal sintering becomes marked at about 600° C.; its onset is somewhat hastened by increase of initial oxygen content. The detailed form of the dilation/temperature curves obtained is explained by the superposition of the several expansions and shrinkages.

Dilation/time curves for isothermal heat-treatments indicate little or no shrinkage at 220° and 435° C., but initially rapid shrinkage at 665°, 755°, and 880° C. The shrinkage rate markedly diminishes with time, but compacts still shrink slowly even after 4 hr. at 880° C. The form of the curves is discussed in terms of current theories of sintering; it is suggested that the ultimate slow shrinkage is limited by the rate of diffusion of trapped gases in closed pores through the metal lattice.

The weight losses of compacts during heat-treatments in hydrogen show that oxide reduction is complete after a 4 hr. treatment at 435° C. or higher. During heat-treatment at 755° C. in argon and nitrogen, oxide vaporizes from the outer layers of the compacts.

Compacts having initial oxygen contents up to 0.53 wt.-% can be sintered to a final density of *c.* 8.5 (volume porosity *c.* 5%), by heating for 4 hr. at 880° C. or 1 hr. at 950° C. For higher initial oxygen contents, the final density decreases, but even cuprous oxide compacts (11.2% of oxygen) shrink by reduction and sintering during 1 hr. at 950° C. to give a final density of 7.8.

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Compacting pressure has only a minor influence on shrinkage rate; its main influence on reduction and sintering shrinkage is indirect—harder-pressed compacts are less porous and have less distance to shrink. Anomalous expansion of certain compacts pressed at 30 tons/in.² is explained by gas inflation due to oxide sealed in by the high pressure.

GENERAL INTRODUCTION.

THE mechanisms of the pressure bonding and the heat sintering of metal powders have been considerably studied, both for complex commercial metal compacts and for simplified cases designed to give fundamental information. It is well established ¹⁻⁶ that compacting involves packing, arrangement, deformation, and fragmentation of the powder particles, and that their bonding is due to a combination of mechanical interlocking and cold welding, the latter occurring when points on the surfaces of two particles are pressed to within atomic distances of each other, perhaps sometimes with highly localized and ephemeral melting. Recent studies of the sintering process for pure metals ⁷⁻¹² have given confirmation of the long-held belief that the driving force of sintering is the surface free-energy decrease that occurs when the total surface area of the pores in the compact diminishes; some authors have suggested that the movement of metal is viscous flow ⁷ or creep, taking place entirely by surface and volume self-diffusion,^{10, 11} but others ¹² have rejected such a mechanism as being too slow to explain observed rates of sintering and believe that the movement is mainly plastic deformation taking place by the dislocation mechanism, surface and volume diffusion being operative only in keeping the surfaces free from the rumpling usual in plastic deformation. In the above work, the influence of oxide films on the powder particles is frequently mentioned as interfering with pressure bonding and modifying the progress of sintering, but no detailed study of the effects produced by differences in the degree of surface oxidation of the powder appears to have been made.

The present paper describes results on the bonding and sintering of variously oxidized electrolytic copper powder. In Part A, the influence of oxide content on the porosity of green compacts is shown, and deductions are made as to the packing effects of oxide during the pressing. In Part B, dilatometric results for the expansions and shrinkages occurring during the sintering of the same compacts in reducing and in inert atmospheres are given, the relation of these dimensional changes to the oxide content and porosity of the green compacts is shown, and the various mechanisms of the changes are elucidated.

A.—INFLUENCE OF OXIDE ON POROSITY OF UNSINTERED COMPACTS.

Metal powders are readily bonded by pressure in the cold; compacts can be prepared from variously oxidized powders and indeed from pure oxides.¹³ Both the density and the breaking strength of unsintered, "green" compacts decrease with increase of the degree of oxidation of the metal powder. Balke¹⁴ found that the green densities of compacts prepared from an iron powder containing a higher amount of oxide were always less than those made from powders of a lower oxide content, though the differences become less marked at high compacting pressures; he did not analyse his results so as to separate the effects due to the different densities of metal and oxide and to any change in porosity with change of oxide content. The results of Eilender and Schwalbe¹⁵ indicate that both the green density and sintered density of iron compacts are increased by decreasing the oxygen content of the iron powder used. However, the various oxide contents were achieved by hydrogen reduction at various temperatures, which introduced the complicating factor of the degree of annealing and softening of the powder. Differences in the amount of residual stress in a powder may lead to differences in the green density of compacts made from it, and it is thus difficult to evaluate the exact influence of oxide films on the effects observed by these workers.

The results given in Part A of the present paper show the influence of oxide films on the porosity of green compacts made from a series of electrolytic copper powders ranging from nearly pure copper to cuprous oxide (11.2 wt.-% of oxygen) pressed at 10, 20, and 30 tons/in.². A tentative explanation of the variation of porosity is given in terms of the likely effects produced by the oxide films in the pressing process.

I.—EXPERIMENTAL TECHNIQUE.

1. *Preparation and Characteristics of Powder.*

The powder used in the whole research was prepared in one batch by the electrolytic method. The bath conditions were similar to those developed by Fitzpatrick, Clark, and Tiernan.¹⁶ The electrolyte, containing 2.35 wt.-% of copper as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 11.5 wt.-% of sulphuric acid, was held in a large conical funnel (Fig. 1). This was connected at the stem by rubber tubing to a flask *A*, which acted as a receptacle for the powder. The flask could be sealed off from the rest of the apparatus by means of a screw clip and subsequently removed; this afforded easy access to the product. Both funnel and flask were

cooled, the former by means of a slow stream of water through the container *B*, the latter by ice and water. The electrolyte was kept in slow circulation by the two stirrers *C*, which were rotated by the motor *D* through a reduction gear *E*.

About 4 l. of electrolyte was roughly deaerated by boiling, nitrogen being bubbled through during the cooling period. The cathode *F*, a cylinder of pure copper 6 in. long \times $1\frac{3}{8}$ in. in dia., and the anode *G*, a tube of pure copper 6 in. long, 3 in. in dia., and $\frac{3}{8}$ in. thick, were partially immersed in the electrolyte, and a current of 40 amp. was passed. This gave an anode c.d. of 75 amp./ft.² and a cathode c.d. of 380 amp./ft.². The flow of water through the cooling vessel *B* was regulated to control the bath temperature at 40°–45° C. The powder was scraped from the cathode at regular intervals and fell into the cooler liquid in the flask *A*, so that oxidation in the warm acid solution was minimized.

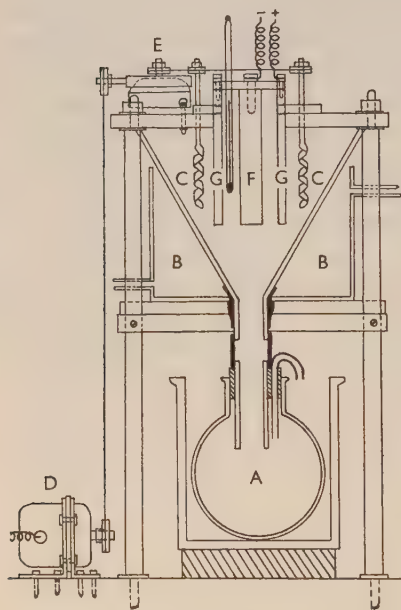


FIG. 1.—Cell for Electrolytic Production of Copper Powder.

the powder removed from the apparatus.

The powder was then separated by decantation, washed with several successive amounts of deaerated distilled water, then with dilute sodium carbonate solution, and finally again with distilled water, as recommended by Hothersall and Gardam.¹⁷ It was then dried in hydrogen at 120° C. and stored in a gas-tight container in an atmosphere of hydrogen.

The oxide content of the powder was low and the particle shape dendritic (see Fig. 23, Plate XLV). The principal characteristics of the powder are given below :

Apparent density	1.266 g./c.c.
Tap density	1.68 g./c.c.
Oxygen content (determined by weight of water produced by heating in hydrogen at 850° C.)	0.28 wt.-%
Flowability (from 60° cone through orifice $\frac{3}{16}$ in. dia. and $\frac{1}{8}$ in. long.)	nil
Particle-Size Distribution :	

— 300 Mesh Fraction

Mesh	Wt.-%	Microns	% of Particles
+ 100	4.0	45-35	4
- 100 + 160	9.9	35-25	25
- 160 + 200	6.2	25-15	53
- 200 + 240	3.2	15-5	16
- 240 + 300	11.1	< 5	2
- 300	65.6

2. Reduction and Controlled Oxidation of Powder.

Preliminary experiments established that the reduction of the existing oxide film on the electrolytic powder could be achieved by heating in hydrogen at 255°-260° C. for about 48 hr. The low temperature was necessary in order to prevent serious agglomeration of the powder. It was also found that the oxidation of the reduced copper powder proceeded at a conveniently rapid rate above about 210° C.; the oxide formed under these conditions was almost entirely cuprous oxide.

The apparatus shown in Fig. 2 was used for the reduction and controlled oxidation of copper powder. A weighed amount of powder, contained in the reaction chamber *A*, was first reduced by heating in a stream of hydrogen at 255°-260° C. for 48 hr. The powder was allowed to cool in an atmosphere of pure dry hydrogen, which was then displaced by a stream of pure dry nitrogen (both gases were passed over copper, nickel, and iron at 650° C. and then over silica gel, solid potassium hydroxide, and phosphorus pentoxide). The reaction chamber was then sealed off at the neck *Y* and evacuated; dry oxygen was then slowly admitted into the apparatus from the graduated reservoirs *B* and *C* until the pressure in *A* was atmospheric. The reaction chamber was then connected to the manometer and the powder heated to 210°-220° C., being held at that temperature until oxidation had proceeded to the required degree as indicated by the oxygen taken up. After the oxidation the reaction chamber was evacuated and refilled with purified nitrogen; the neck *X* was then sealed and the powder kept in the air-tight vessel thus formed until required.

Throughout the reduction and oxidation the powder had to be thoroughly shaken to minimize caking, particularly just before the oxidation was begun, when it was desirable to expose as much of the particle surface to oxygen as possible. It was also essential that the powder should be cold when oxygen was first admitted, in order to

avoid preferential oxidation of the powder nearest to the oxygen supply.

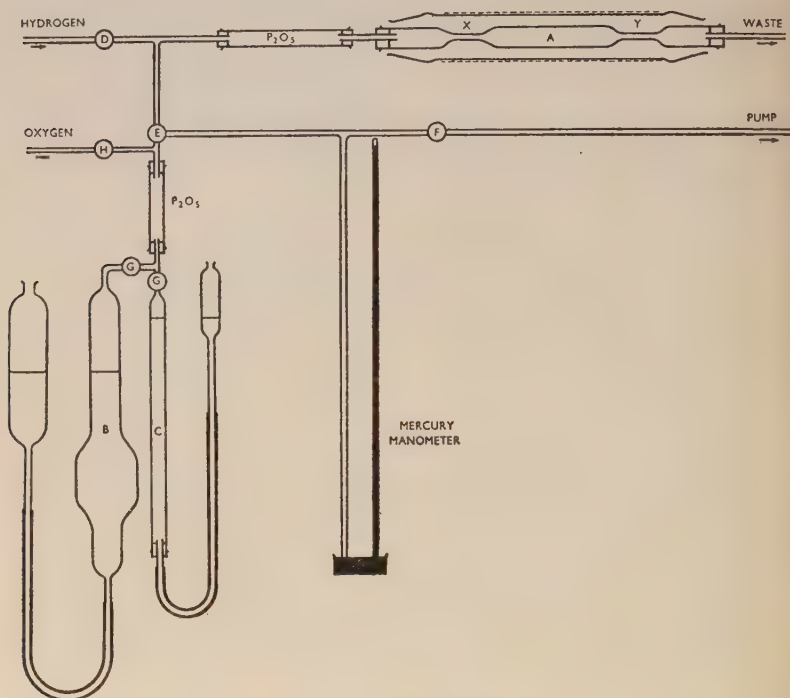


FIG. 2.—Apparatus for Reduction and Controlled Oxidation of Copper Powder.

KEY.

A Reaction chamber. B Large oxygen reservoir. C Small oxygen reservoir.

TABLE I.—*Oxygen Content of Powders.*

By Synthesis	By Analysis		
Oxygen, wt.-%	Oxygen, wt.-%	Cuprous oxide, wt.-% *	Cuprous oxide, vol.-% *
0.10	0.11	0.98	1.45
0.20	0.20	1.79	2.63
0.50	0.53	4.74	6.87
1.00	1.13	12.72	14.29
2.25	2.32	20.73	28.05
5.50	5.76	51.47	61.15
11.20	11.16	99.72	99.84

* On the approximate assumption that all the oxygen is present as stoichiometric Cu_2O .

The oxygen content of the powders could be calculated from the amount of oxygen taken up. In all cases the value was also determined by analysis (weight of water formed by hydrogen reduction at 850° C.) immediately before the powder was compacted and also, on another specimen, immediately after the compacts had been made, so that any oxidation during the exposure to air could be noted. Powders containing 0.11, 0.20, 0.53, 1.13, 2.32, 5.76, and 11.16 wt.-% of oxygen were prepared. Table I shows the very fair agreement between the synthetical and analytical determinations of oxygen content.

The true density of the 0.11% oxygen powder was determined by S.G. bottle, all gas being removed from open porosity by evacuation after the powder had been covered with water. The value obtained, 8.93 g./c.c., agrees precisely with that calculated from the metal and oxide solid densities (8.96 and 6.04 g./c.c., respectively); this shows that the powder contained no closed voids.

3. Production of Compacts.

The oxidized powders were pressed in a high-tensile steel die,* the dimensions of which are shown in Fig. 3. The die cavity was lapped to a mirror finish to reduce wall friction, and two plungers were used for double-action pressing, so that longitudinal density variations in the compacts should be minimized.

* 13% Chromium, 1.5% carbon, 0.5% tungsten, oil-quenched; kindly supplied to our specification by The Manganese Bronze and Brass Co., Ltd.

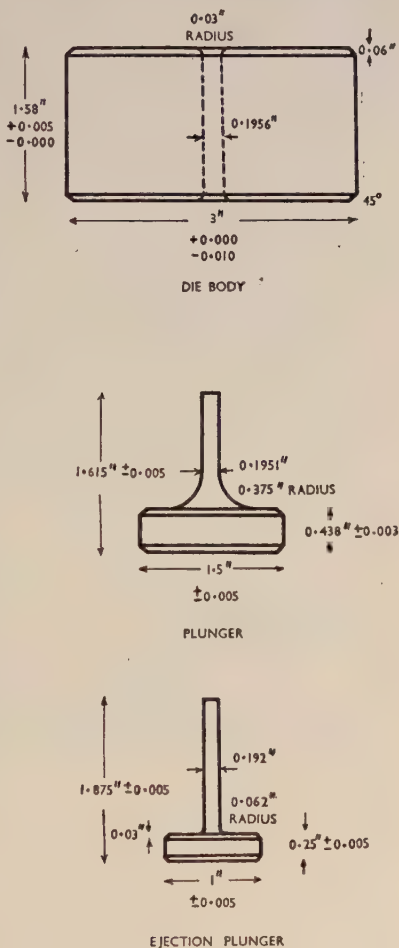


FIG. 3.—High-Tensile Steel Die.

A Hounsfield tensometer with a special attachment* was used for application of pressure. Small springs placed between the die body and the platens of the attachment ensured even pressing from both ends. The rate of loading was controlled by driving this machine through a series of reduction gears, which allowed the trial use of 18 loading speeds. The same programme was finally adopted for all compacting, viz. :

- 30 sec. for loading,
- 30 sec. " dwell time " at pressure,
- 30 sec. for unloading.

No lubricants were used at any stage, and the die was scrupulously cleaned after each compaction.

The amount of powder used for each compact was varied according to the compacting pressure used and the oxygen content of the powder, so that the height of all compacts produced was about 3.5 mm., corresponding to a height/diameter ratio of 1:1.43. Pressures of 10, 20, and 30 tons/in.² were used for compacting, at least three compacts being produced for each oxygen content at each pressure. The dimensions and weight of each compact were measured as soon after compacting as possible, so that any effects of further oxidation would be avoided. The green densities so determined were checked by water-displacement measurements, the compacts being very lightly greased to prevent water penetrating the pores. The results of the two methods were in very fair agreement.

II.—RESULTS AND INTERPRETATION.

The values of the green densities obtained by mensuration (thought to be the more reliable) are given in Table II, each figure being the average of at least three determinations. Values of the specific volume (the reciprocal of the density) and of the porosity in per cent. v/v (calculated by taking the densities of solid copper and solid cuprous oxide as 8.96 and 6.04 g./c.c., respectively) are also included.

It may first be noted that, for any one powder, the green density of compacts increases, and the porosity decreases, with increase of compacting pressure from 10 to 30 tons/in.². This expected effect is the more marked the lower the oxygen content of the powder; probably, powders carrying relatively thick layers of brittle surface oxide crush nearly as readily at 10 as at 30 tons/in.² compacting pressure, so that the relative effect of increasing the pressure from 10 to 30 tons/in.² is

* The standard fittings available for this purpose were too small to admit the die body; consequently a larger but otherwise similar attachment was constructed in the laboratory.

less than in the case of nearly pure copper powders, which may be expected to crush or deform much less readily at 10 than at 30 tons/in.².

The green density of compacts pressed at any one pressure shows a continuous fall with increase of oxygen content from 0.11% (nearly pure copper, solid density 8.96 g./c.c.) to 11.2% (cuprous oxide, solid density 6.04 g./c.c.). The changes of density are not, however, due entirely to change of composition, as may be seen from the values for the porosity of the compacts (Table II), which changes with composition in a far from simple manner.

TABLE II.—*Variation of Density, Specific Volume, and Porosity of Compacts with Oxygen Content.*

Oxygen Content, wt.-%	Green Density, g./c.c.			Specific Volume, c.c./g.			Porosity, % (v/v)		
	Compacting Pressure, tons/in. ²								
	10	20	30	10	20	30	10	20	30
0.11	5.98	7.04	7.60	0.167	0.142	0.132	33.0	21.2	14.9
0.20	5.81	6.80	7.30	0.172	0.147	0.137	34.8	23.7	18.1
0.53	5.56	6.56	7.04	0.180	0.152	0.142	37.0	25.6	20.2
1.13	...	6.42	0.156	25.9	...
2.32	5.41	6.27	6.72	0.185	0.160	0.149	35.2	25.0	19.6
5.76	4.92	5.62	6.00	0.204	0.178	0.167	34.0	24.6	19.5
11.2	4.00	4.47	4.78	0.250	0.224	0.209	33.8	26.1	20.9

A physical picture of the results of the compacting process for the different powders at different pressures can be better obtained from a consideration of the change of specific volume of the compacts with oxygen content, than from the conventional density and porosity figures. In Fig. 4 (a), (b), and (c) the specific volumes of the compacts are plotted against oxygen content for the three compacting pressures used.

It will be convenient to consider the results for 20 tons/in.² compacting pressure (Fig. 4 (b)) first. Line *A* in this diagram shows the experimentally determined specific volumes. Line *B* shows the variation of specific volume with oxygen content for copper/cuprous oxide mixtures having no voids or porosity, derived from the specific volume values for the solid metal and solid oxide, 0.112 c.c./g. and 0.166 c.c./g., respectively. The point at which line *C* intersects the vertical broken line represents the experimentally determined value of the specific volume of compacted cuprous oxide powder (11.2 wt.-% oxygen); line *C* is derived from this point for copper/cuprous oxide compacts *on the assumption that their porosity is the same as that of pure cuprous oxide compacts*. The point *d* on line *D* is the specific volume of compacted oxygen-free copper powder, obtained by extrapolation of the

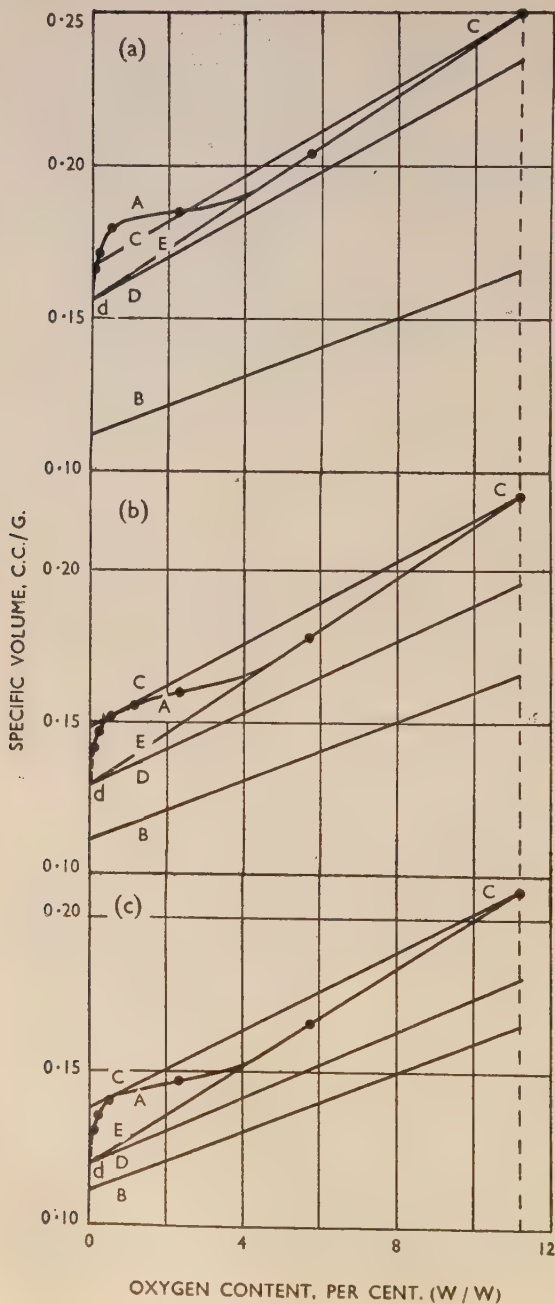


FIG. 4.—Variation of Specific Volume of Green Compacts with Oxygen Content. Compacting pressure :

(a) 10 tons/in.²;

(b) 20 tons/in.²;

(c) 30 tons/in.².

experimental values for the low-oxygen copper powders; line *D* is derived from this point for copper/cuprous oxide compacts *on the assumption that their porosity is the same as that of pure copper compacts*. Line *E* is derived on the assumption that the specific volume of copper/cuprous oxide compacts varies rectilinearly from that of copper to that of cuprous oxide as the composition varies from 0 to 100% of cuprous oxide. It will be seen that, as the oxygen content is increased, the specific volume at first increases rapidly from that associated with pure copper compacts to that associated with compacts having the porosity of cuprous oxide compacts (line *C*). It afterwards continues to rise, but more slowly, approaching that associated with compacts containing copper and cuprous oxide, each contributing its own particular porosity (line *E*), at compositions corresponding to about 40–50 wt.-% of cuprous oxide.

These results may be tentatively explained as follows. At high oxygen contents, the compacting process splits off the relatively thick, brittle layer of cuprous oxide from each copper particle, and the particles of oxide and metal pack in such a manner that each constituent may be regarded as contributing its own particular porosity, due to its especial size, shape, "crushability", and so forth. At moderate oxygen contents, the relatively thin layer of cuprous oxide on each particle, supported by the underlying copper, does not split off, and such crushing as occurs is almost entirely of the particles as a whole. The crushed particles retain substantially a cuprous oxide surface, and consequently pack much more in the manner of cuprous oxide than in that of copper, with much less cold welding and more resultant porosity. At still lower oxygen contents, the very thin cuprous oxide film is penetrated at many points and copper-to-copper bonding and packing rapidly gains in importance.

In the case of the compacts pressed at 10 tons/in.² (Fig. 4 (*a*)), it will be noticed that the specific-volume/composition curve rises above line *C* for powders of moderate oxygen contents—in other words these powders pack less well even than cuprous oxide. This anomaly may well arise because the low compacting pressure, while still sufficient to split off and shatter cuprous oxide particles and produce their usual packing, is insufficient to break or bend copper particles carrying only a thin oxide film to anything like the extent found at higher pressures or with more oxidized particles. Thus relatively large, oxide-coated particles remain after pressing, with the result that the specific volumes and porosities of these compacts (at the copper end of the series pressed at 10 tons/in.²) are abnormally high compared with those of all other compacts here reported.

III.—DISCUSSION.

The abnormally high and rapidly varying porosities and specific volumes found in compacts containing 0.1–3.0 wt.-% of oxygen are of some practical interest, since commercial copper powders have oxygen contents within this range. It is shown in Part B, however, that the sintering shrinkage of such compacts is also abnormally high, so that the net effect produced by oxide variation upon the density of sintered compacts is much less than that upon the density of green compacts.

The considerable influence of oxide films upon the compacting of copper powder is also of interest in connection with the use of copper powders variously coloured by oxidation for the visual indication of density distribution in green compacts;⁴ the present results indicate that the method may be unreliable.

It should be emphasized that the results now reported refer only to dendritic electrolytic copper powder: their supplementation with results for the much more nearly equi-axed powders made by reduction or atomizing would be of much interest.

B.—INFLUENCE OF OXIDE ON DIMENSIONAL CHANGES DURING SINTERING OF COMPACTS.

The length and volume changes that accompany the heat-treatment of metal-powder compacts have frequently been used as a means of studying the progress of sintering.¹⁸⁻²¹ Measurements of dimensions before and after the sintering treatment, such as those of Drapeau,¹⁹ include changes that occur during the heating and cooling of the compacts as well as those that take place during any isothermal sintering, and an analysis of the sintering process based on such results is rendered difficult by the lack of differentiation between the parts of the process.

The advantages of a dilatometric method whereby dimensional changes may be recorded continuously throughout the process are apparent, though until recently little use has been made of this technique. Trzebiatowski,²² studying the sintering process in copper and gold compacts mainly by electrical measurements, made a few dilatometric experiments of which the results, as far as they go, are in harmony with those of electrical conductivity. Kalischer²³ used a dilatometer to study the influence of particle size on the sintering process for various metal compacts. He found an initial thermal expansion similar to that of solid metal, followed by a shrinkage caused by the reduction of the porosity of the compacts associated with sintering. The temperature at which shrinkage began depended on the metal used. An anomalous effect was obtained in one case, that of cobalt, which gave an initial

coefficient of expansion much larger than that of the solid metal. Duwez and his co-workers²⁴⁻²⁶ have recently made extensive dilatometric studies of the sintering process. Of particular interest is the work of Duwez and Martens,²⁶ who studied the influence of heating rate and that of compacting pressure. They found that, for heating rates up to 10° C./min., the initial expansion of their copper compacts closely approximated to that of solid copper, after which shrinkage set in. The onset of shrinkage occurred at approximately the same temperature for each heating rate, although the amount of shrinkage at any higher temperature increased with decrease of the heating rate. Increase of compacting pressure raised the temperature required for the onset of shrinkage and led to slower and less extensive shrinkage. An anomalous expansion was observed in compacts of one particular copper powder at high compacting pressures; this result was attributed to the expansive effects of closed gas pockets in the original powder particles.

In the present work, the influence of the oxide content of electrolytic copper powder on the sintering process has been studied. The following sections describe dilatometric results on the expansions and shrinkages that occur during the heating-up of compacts, and on the rate of shrinkage during isothermal sintering, in reducing and in inert atmospheres. These results, together with weight and dimensional measurements of the green and sintered compacts, and microscopic examination of selected sintered compacts, have enabled a fairly complete picture of the direct and indirect influences of oxide on the sintering process to be drawn.

I.—EXPERIMENTAL TECHNIQUE.

Sintering experiments were carried out in a photographically-recording differential dilatometer of the well-known Chevenard type. As atmospheres other than air were required, the instrument was modified as shown in Fig. 5. The housing of the dilatometer optical system, *B*, was made gas-tight by sealing a circular, flat piece of glass over the open end, and a $\frac{1}{4}$ -in.-dia. brass tube was screwed into the side of the housing. Gas passed in through this tube and out through the holes carrying the silica push-rods into the specimen-tube of the dilatometer. This tube was heated by sliding a wire resistance furnace *C* over it. Owing to the large difference in the diameters of the furnace- and specimen-tubes on the unmodified instrument, and also to the fact that the furnace casing extended almost to the ends of the furnace tube, it was impossible to make a gas-tight joint directly between the furnace tube and the specimen-tube. Accordingly, a silica tube was put through the furnace, of such dimensions that it slipped easily over

the specimen-tube and projected out of the furnace for several inches at each end. One end was sealed on to the specimen-tube by means of a large rubber stopper bored to a tight fit over the specimen-tube and countersunk at one end to give a tight fit over the long silica tube (Fig. 5); this joint was made gas-tight with silicone vacuum grease. The other end of the long silica tube was sealed by a rubber stopper carrying a glass T-joint, made gas-tight with picein. Copper tubes wound round both ends of the long silica tube carried cold water to keep the gas-tight joints cool.

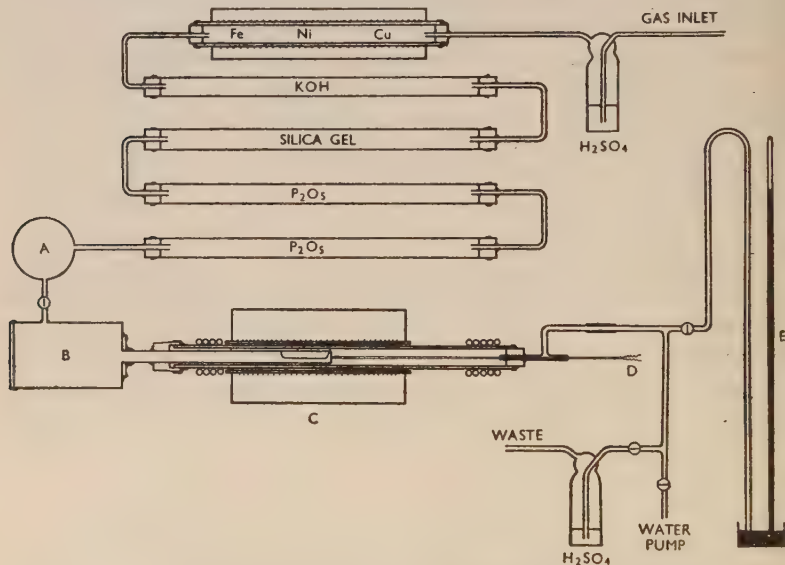


FIG. 5.—Dilatometric and Ancillary Apparatus.

KEY.

A Flowmeter. B Optical system. C Dilatometer.
D Thermocouple. E Manometer.

Hydrogen, argon, nitrogen, and carbon monoxide used for the sintering atmospheres were purified by passing them over copper, nickel, and iron gauzes at 650° C. and then over solid potassium hydroxide, silica gel, and phosphorus pentoxide. A capillary flowmeter *A** (Fig. 5), similar in principle to that described by Pourbaix,²⁷ was used to measure the rate of gas flow. A water-pump was attached to the exit end of the furnace so that air in the apparatus could be rapidly removed and replaced by the desired gas.

A further modification of the dilatometer was necessitated by the

* See Appendix I (p. 389).

sensitivity of the recording device, which, based on an optical-lever system worked by the differences in expansion of the test specimen and a standard specimen of Pyros lying immediately above it, gives a magnification factor of about 300 times. The relatively large length changes that take place during sintering are thus impossible to record if the compact is of the standard dilatometer specimen length, 5 cm. Compacts 0.35 cm. long were therefore produced as described in Part A, and the total specimen length was made up to 5 cm. by means of a Pyros piece of adjustable length (Fig. 6). This was machined from the same sample of Pyros as the bar used for the standard

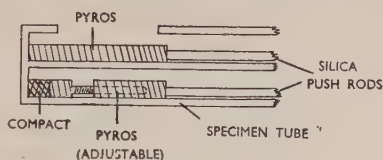


FIG. 6.—Detail of Test Specimen.

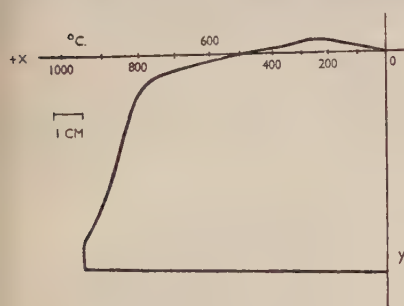


FIG. 7.—Typical Dilatometer Record.

specimen, and gave satisfactory results when calibrated against pure copper and Invar bars. Appendix II (p. 390) shows the method by which absolute changes of compact length were calculated from the photographic record obtained with the above arrangements.

Experiments were made using heating rates of 5°, 20°, and 30° C./min., controlled by the standard clockwork-thermo-regulator

device on the dilatometer. For isothermal sintering, an attachment moving the recording photographic plate at a constant rate, standard to the instrument, was used to record changes of specimen length with time. All compacts were weighed, and measured by micrometer, before and after sintering. All experiments were performed in duplicate.

II.—RESULTS AND INTERPRETATION.

1. Heating in Hydrogen Atmosphere.

(a) Dimensional Changes during Rise of Temperature.

Compacts of the seven powders of varying oxygen content, pressed at 20 tons/in.², were heated in hydrogen in the dilatometer from 20° to 950° C. at rates of 5° and 30° C./min.; a few experiments were also made at a heating rate of 20° C./min. A typical dilatometer record is shown in Fig. 7; from such traces the absolute percentage

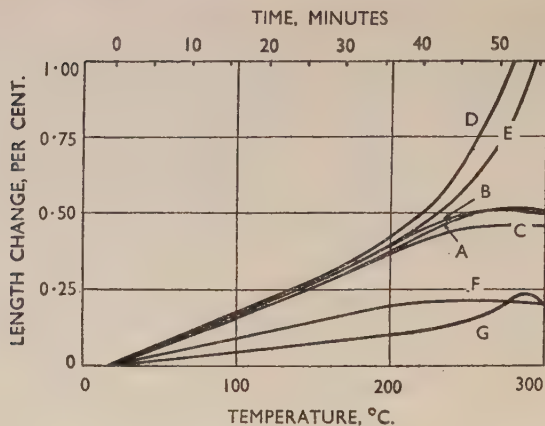


FIG. 8.—Length Changes during Temperature Rise (Early Stages). Heating rate: 5°C./min. Initial oxygen content: A 0.11, B 0.20, C 0.53, D 1.12, E 2.32, F 5.76, G 11.2 wt.-%.

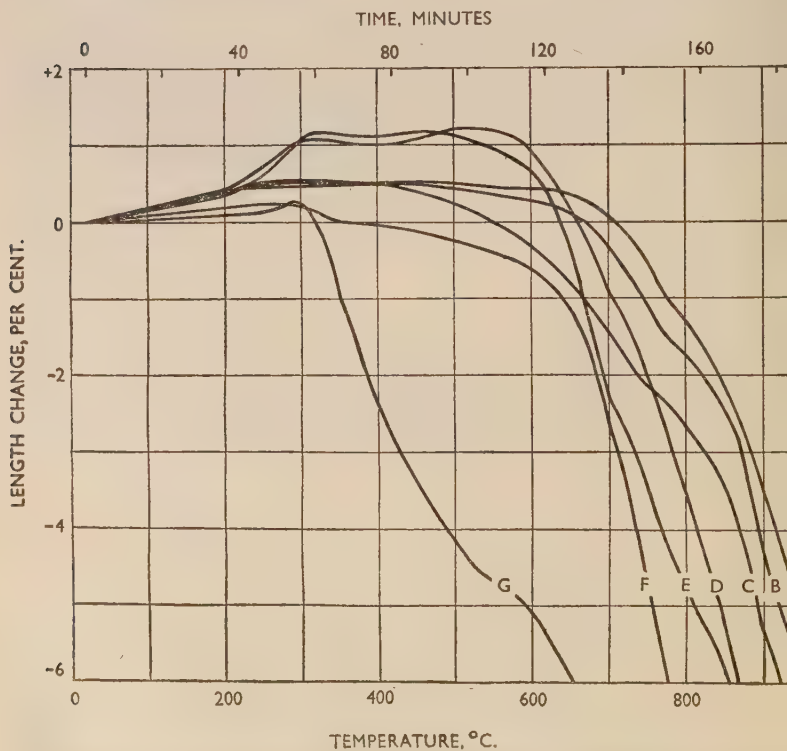


FIG. 10.—Length Changes during Temperature Rise. Heating rate: 5°C./min. Key as Fig. 8.

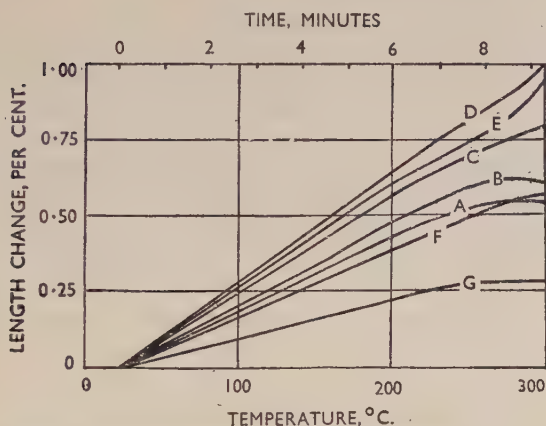


FIG. 9.—Length Changes during Temperature Rise (Early Stages). Heating rate: 30°C./min. Key as Fig. 8.

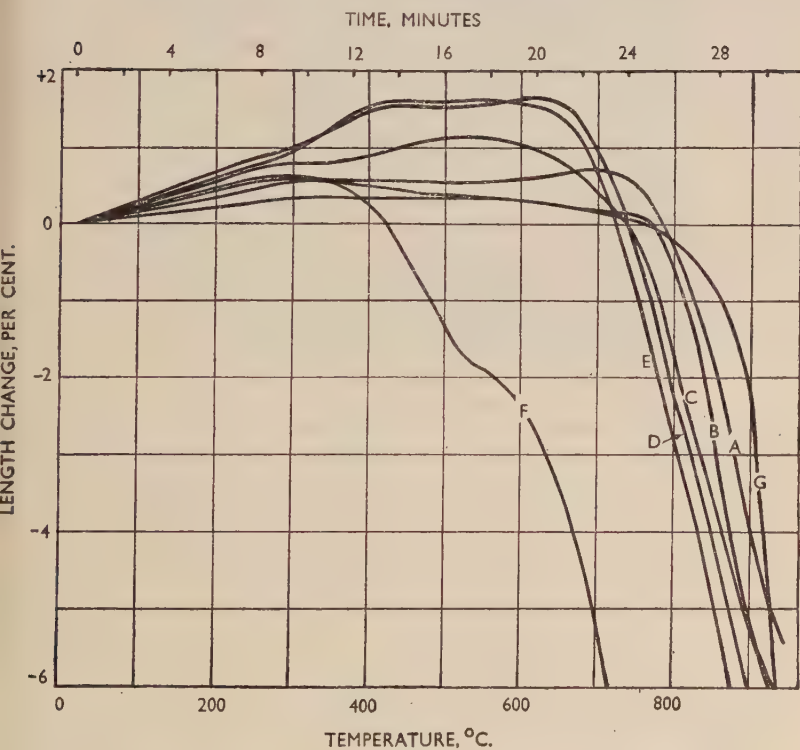


FIG. 11.—Length Changes during Temperature Rise. Heating rate: 30°C./min. Key as Fig. 8.

change of length of the compact at each time and temperature has been calculated by the method given in Appendix II (p. 390). The results, given graphically in Figs. 8–11, show that all the compacts underwent an initial extension followed by a very marked shrinkage.

It is convenient first to consider the extensions, shown on a large scale in Figs. 8 and 9. Up to 200°C . (250°C . in the case of the faster heating rate), the extension of each compact is a rectilinear function of temperature; the gradients of the extension/temperature lines are apparent coefficients of thermal linear expansion, and are plotted in Fig. 12 against oxygen content. The dotted line in this diagram represents the weighted mean of the thermal expansion coefficients of copper (16.6×10^{-6} cm./cm./ $^{\circ}\text{C}$.) and cuprous oxide (0.9×10^{-6}

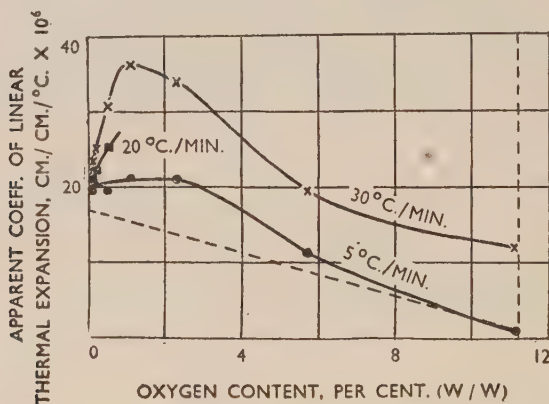


FIG. 12.—Variation of Apparent Coefficient of Thermal Linear Expansion with Initial Oxygen Content, for Three Heating Rates.

cm./cm./ $^{\circ}\text{C}$.), respectively, and gives a rough indication of the coefficients to be expected for non-porous mixed compacts of metal and oxide. It will be seen that all the compacts (except that made of pure cuprous oxide, heated slowly) show apparent expansion coefficients considerably greater than those that might be expected if the expansion were due only to true thermal expansion of the metal and oxide, and that the extra expansion is greater for the more rapid rate of heating and maximal at oxygen contents in the region of 1–2 wt.-%. Fig. 13 shows the porosities of the green compacts (Table II, Part A) plotted against oxygen content, and a comparison between this diagram and Fig. 12 shows that the extra expansion is correlated with the porosity of the green compact, compacts having the highest porosity giving the greatest extra expansion. The effect is thus undoubtedly

due to an inflation of the mechanically weak green compacts by the thermal expansion of gas entrapped in voids; it is the more marked at the faster heating rate because of the lessened opportunity for gas to escape.

The expansion becomes even more marked for the 1.13 and 2.32% oxygen compacts (curves *D*, *E*) between 200° and 300° C. for slow heating, and between 350° and 440° C. for rapid heating (Figs. 8 and 9.) This effect is probably due to the production of steam in the voids by the onset of reduction of oxide by hydrogen; since hydrogen can diffuse

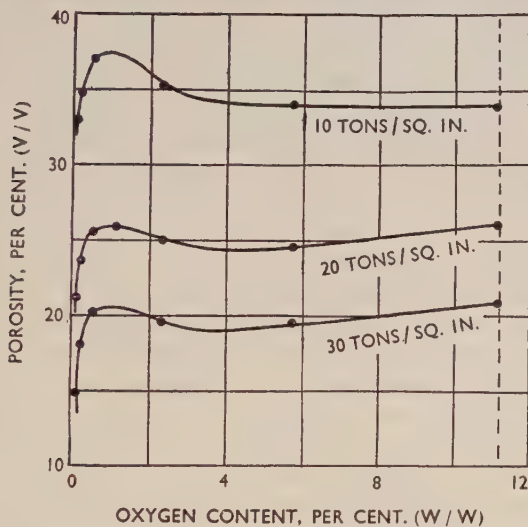


FIG. 13.—Variation of Porosity of Green Compacts with Oxygen Content, for Three Compacting Pressures.

into the compact much more rapidly than steam can diffuse out, this enhances the inflation of the compact. At slightly higher temperatures, a minor shrinkage and another small expansion occur; it is probable that the inflated compact partially bursts (like a slightly overdone soufflé), releasing gas, and then shrinks owing to the continuing reduction of oxide to the less voluminous metal and to the beginning of sintering, whereafter a further small expansion takes place. The steam-expansion effect is smaller in the low-oxygen compacts (curves *A*, *B*, *C*) because less steam is there produced, and is also minor in the high-oxygen compacts (curves *F*, *G*) because these especially weak compacts burst the most readily. With all compacts, however, it is evident from the form of the curves that there is a heating range, usually

considerable, over which the thermal and inflation expansion effects are approximately balanced by the shrinkages caused by reduction and, eventually, sintering.

The final large and rapid shrinkage caused by sintering and reduction sets in, with the exceptions discussed below, at temperatures in the range 550° – 750° C. (Figs. 10 and 11). In general, increase of oxygen content in the compact leads to the shrinkage beginning sooner and at a lower temperature, and proceeding to a greater extent (see next section), undoubtedly because of the greater contribution of the reduction process and (in the range of low oxygen contents) to the greater porosities of the green compacts. Reduction shrinkage of the cuprous oxide compact (curve *G*) begins at about 300° C. when it is heated slowly (Fig. 10), but only at 800° C. when it is heated rapidly (Fig. 11); this anomaly may well be due to the initial lack of metallic nuclei in this compact, for it is well known that there can be a period of induction before reduction of cuprous oxide begins unless a $\text{Cu}_2\text{O}/\text{Cu}$ interface is present.²⁸

The curves obtained at the slower rate of heating (Fig. 10) show an inflection during the rapid-shrinkage period; this inflection occurs the sooner, and thus at a lower temperature, the greater the oxide content of the compact. It is likely that the oxide actually influences the *time required* for the compact to reach the condition leading to the partial arrest and subsequent acceleration of shrinkage, rather than that it directly influences the temperature at which it occurs, and a possible explanation of the effect is as follows. The first step in the reduction of an oxide film on a copper particle is the removal of oxide ions from the surface of the oxide by adsorbed hydrogen molecules, with the formation of water and the setting free of electrons in the conduction band of the oxide. Cuprous ions and electrons then either produce metallic nuclei in the surface of the film, as shown by Garner, Gray, and Stone,²⁹ or migrate through it to the copper already present at the film/metal interface. The first of these parallel and competing reactions leads after a time to the production of a continuous copper film on the outside of the oxide layer; this film restricts hydrogen access to the oxide, slowing down the reduction, but, since hydrogen can diffuse through it, does not stop the reduction entirely. Steam formed below the metal film cannot escape until it has built up a pressure sufficient to disrupt the film, whereupon reduction accelerates again. Now, the thicker the initial oxide film, the slower is the diffusion of cuprous ions and electrons to the original oxide film/metal interface. Consequently, the growth of the external metal film is faster, and thus compacts with the larger oxide contents show the inflection effect after shorter periods.

(b) *Dimensional Changes during Isothermal Treatment.*

Compacts of the powders containing 0.11, 0.20, and 0.53 wt.-% of oxygen (the most interesting compositions from the practical aspect), pressed at 10, 20, and 30 tons/in.², were heated in hydrogen in the dilatometer at various temperatures for 4 hr. In each case the compact was taken up to temperature at 20° C./min.

Typical dilation/time curves for compacts of the three powders pressed at 20 tons/in.² and isothermally treated at 220°, 435°, 665°, 755°, and 880° C. are shown in Fig. 14 (a), (b), and (c).

It will be seen that at 220° and 435° C. little change occurs apart from a slight shrinkage due to oxide reduction. At the higher temperatures, however, the rate of isothermal shrinkage is at first high, but it decreases with increase of time. For all compacts, the higher the temperature the greater is the eventual shrinkage (see also next section).

The results are complicated by the changes during the heating period, already discussed; by the beginning of the isothermal treatment there has usually been a considerable shrinkage, and the higher the temperature of the isothermal treatment (i.e. the longer the heating period) the greater the shrinkage that has occurred before it begins. Nevertheless, the isothermal curves indicate that shrinkage, initially rapid owing to the closing up of the many minute pores and channels in the compact, soon slackens considerably, doubtless because most of the smaller pores and channels have been sealed.

Part of the shrinkage is undoubtedly due to oxide reduction; the curves for compacts containing 0.11 wt.-% oxygen all lie above the corresponding ones for those containing 0.20%. The shrinkages of these latter compacts are, however, *greater* than those of compacts containing 0.53 wt.-% oxygen, for sintering temperatures of 755° C. and below, although at 880° C. the shrinkage of the compact containing 0.53% oxygen becomes greater than that of the compact containing 0.20%. These results show the importance of the changes occurring early in the heating period (see above), and the smaller shrinkage values observed at the lower temperatures for the most highly oxidized powder may be attributed directly to the larger previous expansion. In fact, it is clear that the net shrinkage during isothermal treatment is the resultant of four terms: (i) extension due to gas expansion, (ii) extension due to gas production, (iii) shrinkage due to reduction of oxide, (iv) shrinkage due to sintering. The relative importance of these depends upon the heating rate, the oxygen content of the powder, and the time and temperature of the heat-treatment. For high heating rates, low temperatures of isothermal treatment, and an oxygen content of 0.53 wt.-%, large expansions occur during the heating period, and it is pos-

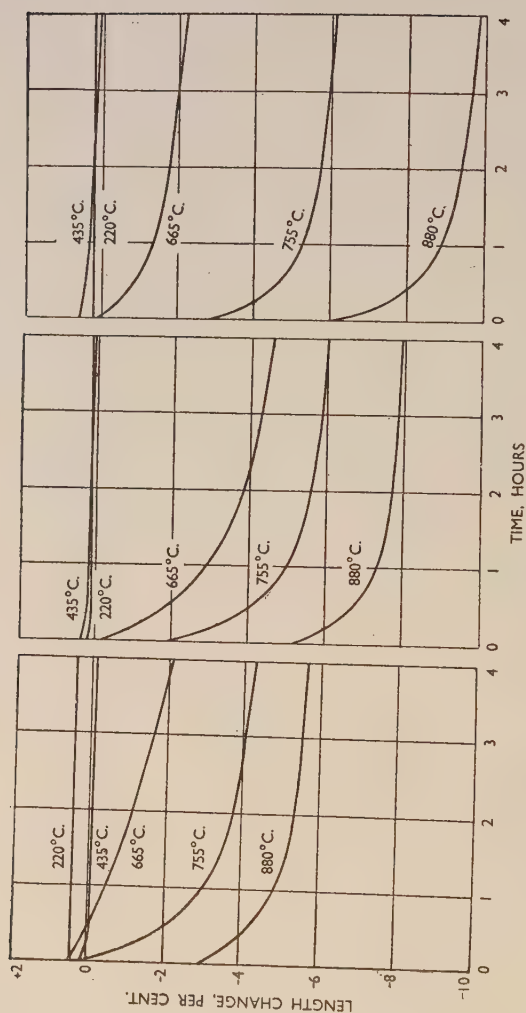


Fig. 14.—Length Changes during Isothermal Heat-Treatments. Compacting pressure : 20 tons/in.².
Initial oxygen content : (a) 0.11, (b) 0.20, (c) 0.53 wt.-%.

sible that even though all the oxide present be reduced to metal, an overall increase in length may result. As the temperature of isothermal treatment is raised, the expansions are eliminated by the larger shrinkages due to increasing sintering. It may be calculated that at the highest temperature used in these experiments, viz. 880° C., the shrinkage after 4 hr., when due allowance has been made for the volume change due to reduction of oxide, is nearly proportional to the porosity of the green compacts (see Table II, Part A). This shows that the expansions associated with the heating period can be quickly overcome under conditions that promote rapid sintering.

The influence of compacting pressure on the sintering process seems to be exerted indirectly through its influence on the porosity of the green compacts. Typical dilation/time curves for compacts containing initially 0.11, 0.20, and 0.53 wt.% of oxygen, pressed at 10, 20, and 30 tons/in.² and isothermally treated at 755° C., are shown in Fig. 15 (a), (b), and (c). It will be seen that, in general, increase of compacting pressure from 10 to 30 tons/in.² leads to slower and less extensive shrinkage (cf. Duwez and Martens²⁶), evidently because the less porous green compacts have a smaller possible volume change and also allow less ready oxide reduction. These factors seem to outweigh any encouragement of sintering by the greater residual stresses in the more heavily pressed compacts.

One set of compacts only, made from powder containing 0.20 wt.-% oxygen pressed at 30 tons/in.², expanded during isothermal heating at 755° C. (Fig. 15 (b)). A unique dilation/temperature curve showing a yet further expansion following the second hump in the curve (cf. Figs. 10, 11) was also obtained with these compacts during the heating period. This result may be tentatively explained as follows: In compacts containing very small amounts of oxide, corresponding to about 0.1 wt.-% oxygen and less, the amount of water vapour produced by reduction of oxide is small and escapes from the compact before the pores leading to the surface become sealed. In compacts containing large amounts of oxide, a large inflation leading to bursting occurs; this, together with reduction of oxide, opens the pores and connecting channels in the compact, ingress of hydrogen and egress of water vapour is facilitated, and shrinkage due to reduction of oxide and sintering occurs normally. In compacts containing a critical amount of oxide, however, apparently that corresponding to 0.20 wt.-% oxygen, the opening of the pores is not sufficient (provided the high compacting pressure of 30 tons/in.² has been used) to allow complete reduction before the sealing action of sintering becomes operative. Oxide is thus sealed into the compact, and its eventual reduction, taking place by

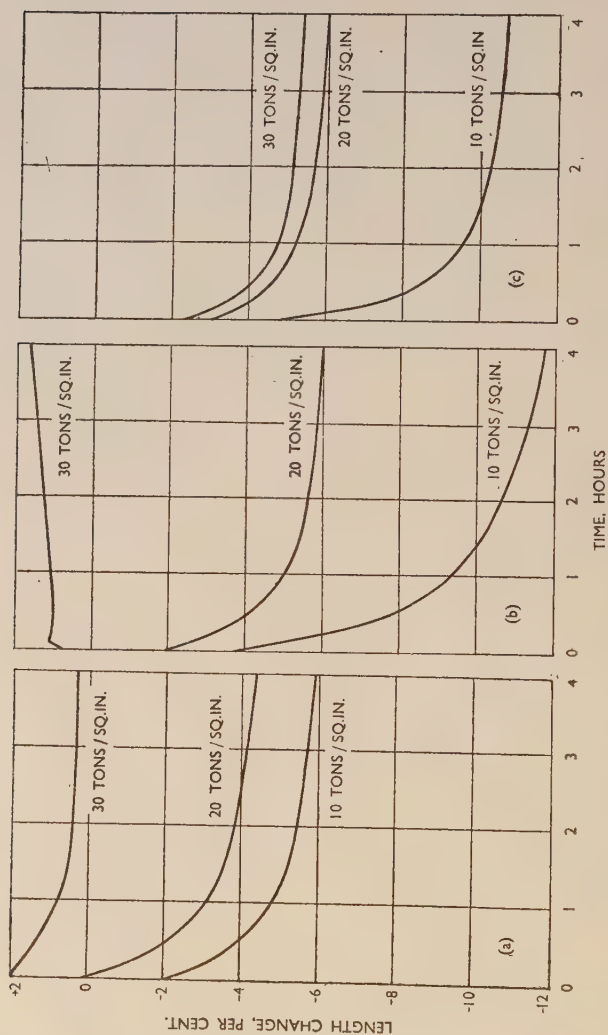


FIG. 15.—Length Changes during Isothermal Heat-Treatment at 755° C. for Three Compacting Pressures. Initial oxygen content : (a) 0.11, (b) 0.20, (c) 0.53 wt.-%.

diffusion of hydrogen through the copper lattice, liberates water vapour, which cannot easily escape and consequently causes an expansion of the compact.

(c) *Overall Changes Produced by Complete Sintering Process.*

The weight losses of the compacts heat-treated as described in the two previous sections are given as percentages of the initial weights in Table III (a) and (b); excellent agreement between duplicate specimens is evident.

TABLE III (a).—*Variation with Initial Oxygen Content of Weight Loss during Heat-Treatment in Hydrogen for Compacts Pressed at 20 tons/in.².*

Heat-Treatment: (A) Heated to 950° C. at 5° C./min., held there for 1 hr., cooled to 20° C. at c. 30° C./min.

(B) As (A) but heated at 30° C./min.

(C) Heated to temperatures indicated at 20° C./min., held there for 4 hr., cooled to 20° C. at c. 30° C./min.

Oxygen Content, wt.-%	Weight Loss during Heat-Treatment, %						
	A	B	C				
			220° C.	435° C.	665° C.	755° C.	880° C.
0.11	0.1	0.1	0.0	0.1	0.1	0.2	0.1
	0.1	0.2	0.0	0.1	0.1	0.1	0.1
0.20	0.2	0.2	0.1	0.2	0.2	0.2	0.3
	0.2	0.2	0.1	0.2	0.2	0.3	0.2
0.53	0.6	0.6	0.3	0.6	0.5	0.7	0.5
	0.5	0.6	0.0	0.7	0.6	0.6	0.7
1.13	1.0	1.2
	1.2	1.2
2.32	2.3	2.4
	2.4	2.3
5.76	5.5	5.8
	5.8	5.8
11.2	12.1	11.9
	11.9	11.7
	...	11.8

Comparison of the figures with those for the initial oxygen content shows close agreement, indicating that complete reduction with removal of oxygen as steam occurred, except in the case of compacts heated for 4 hr. at the lowest temperature, 220° C. The percentage weight-loss figures show, in fact, some tendency to be slightly higher than the

TABLE III (b).—*Variation with Initial Oxygen Content of Weight Loss During Heat-Treatment in Hydrogen for Three Compacting Pressures.*

Heat-Treatment : Heated to 755° C. at 20° C./min., held there for 4 hr., cooled at c. 30° C./min.

Oxygen Content, wt.-%	Weight Loss during Heat-Treatment, %		
	Compacting Pressure, tons/in. ²		
	10	20	30
0.11	0.1 0.2	0.2 0.1	0.2 0.1
0.20	0.3 0.2	0.2 0.3	0.2 0.2
0.53	0.9 0.6	0.7 0.6	0.8 0.6

oxygen-content figures determined for the original powders; this may well be due to unavoidable loss of material during handling of the weak green compacts—the excess loss is, significantly, greatest for the cuprous oxide compact.

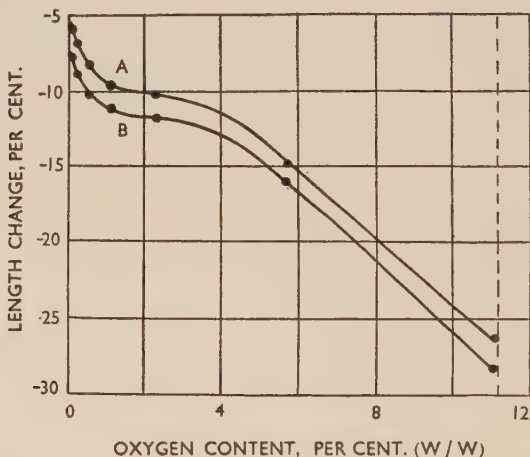


FIG. 16.—Variation of Ultimate Length Change with Initial Oxygen Content. Compacts pressed at 20 tons/in.², heated to 950° C. at 5° and 30° C./min., held there for 1 hr., and cooled at c. 30° C./min. Heating rate: A 30° C./min.; B 5° C./min.

The length changes of the complete series of compacts (pressed at 20 tons/in.²) heated at the two rates to 950° C. and held there for 1 hr.

are plotted (as percentages of the initial lengths against initial oxygen content) in Fig. 16. The considerable increase of shrinkage as the oxide content is increased from nearly zero to 100% is to be expected, and it may also be noted that there is a dip in the shrinkage/oxygen-content curve in the range of 0.11–c. 3% oxygen content, corresponding to the abnormally high porosities and specific volumes of the green compacts in this range, described in Part A. Evidently the heat-treatments, as well as giving complete oxide reduction, are sufficient to diminish the

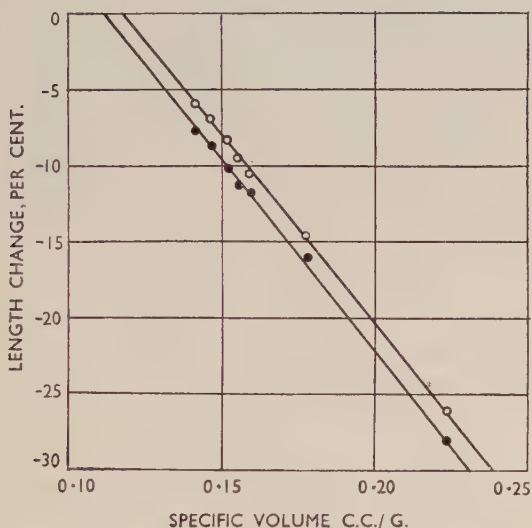


FIG. 17.—Variation of Ultimate Length Change with Initial Specific Volume. Compacts pressed at 20 tons/in.², heated to 950° C. at 5° and 30° C./min., held there for 1 hr., and cooled at c. 30° C./min. Heating rate: ○ 30° C./min.; ● 5° C./min.

porosities of all the compacts to values much more nearly constant than those found in the green compacts. When the percentage length shrinkages are plotted against initial specific volume, as shown in Fig. 17, straight lines are obtained; this fortuitously simple relationship is of interest in that it provides a simple empirical method for predicting sintering shrinkage from green-density determinations. Similar relationships, although not necessarily rectilinear, may exist for other compacts and other heat-treatments: their determination in particular cases might prove convenient in practice. Extrapolation of the straight line found in the present case for the slower heating rate to zero shrinkage indicates that a compact giving no shrinkage would have an initial

specific volume of about 0.11; it is significant that this is the specific volume of pure non-porous copper.

The length changes of compacts containing 0.11, 0.20, and 0.53 wt.-% of oxygen, pressed at various pressures and heat-treated isothermally at the five temperatures, are given in Table IV (a) and (b).

TABLE IV (a).—*Variation with Initial Oxygen Content of Length Change during Heat-Treatment in Hydrogen for Compacts Pressed at 20 tons/in.².*

Heat-Treatment: Heated to temperatures indicated at 20° C./min., held there for 4 hr., cooled to 20° C. at c. 30° C./min.

Oxygen Content, wt.-%	Length Change * during Heat-Treatment, %				
	220° C.	435° C.	665° C.	755° C.	880° C.
0.11	+0.1	-0.5	-3.7	-5.1	-6.8
0.20	-0.2	-0.1	-5.0	-7.3	-8.9
0.53	+0.1	-1.6	-2.8	-6.2	-10.4

* Means of concordant duplicates.

TABLE IV (b).—*Variation with Initial Oxygen Content of Length Change during Heat-Treatment in Hydrogen for Three Compacting Pressures.*

Heat-Treatment: Heated to 755° C. at 20° C./min., held there for 4 hr., cooled to 20° C. at c. 30° C./min.

Oxygen Content, wt.-%	Length Change * during Heat-Treatment, %		
	Compacting Pressure, tons/in. ²		
	10	20	30
0.11	- 6.6	- 5.1	- 0.4
0.20	- 11.2	- 7.3	+ 0.9
0.53	- 12.2	- 6.2	- 6.4

* Means of concordant duplicates.

The general trend for shrinkage to be greater at greater oxygen contents is again to be seen. For any one oxygen content, shrinkage increases with increasing sintering temperature. Shrinkage, for the isothermal treatment at 755° C., in general decreases with increasing compacting pressure; the actual length gain for 0.20% oxygen compacts pressed at 30 tons/in.² after this treatment has already been noted in the dilation/time curves.

TABLE V (a).—*Variation with Initial Oxygen Content of Density after Heat-Treatment in Hydrogen for Compacts Pressed at 20 tons/in.².*

Heat-Treatment : (A) Heated to 950° C. at 5° C./min., held there for 1 hr., cooled to 20° C. at c. 30° C./min.

(B) As (A) but heated at 30° C./min.

(C) Heated to temperatures indicated at 20° C./min., held there for 4 hr., cooled to 20° C. at c. 30° C./min.

Oxygen Content, wt.-%	Density * after Heat-Treatment, g./c.c.						
	A	B	C				
			220° C.	435° C.	665° C.	755° C.	880° C.
0.11	8.6	8.2	7.1	7.1	7.6	8.1	8.6
0.20	8.6	8.0	6.9	7.0	7.8	8.1	8.4
0.53	8.5	8.3	6.6	6.7	7.3	8.0	8.4
1.13	8.1	8.0
2.32	7.9	7.9
5.76	8.0	8.0
11.2	7.8	7.0

* Means of concordant duplicates.

TABLE V (b).—*Variation with Initial Oxygen Content of Density after Heat-Treatment in Hydrogen for Three Compacting Pressures.*

Heat-Treatment : Heated to 755° C. at 20° C./min., held there for 4 hr., cooled to 20° C. at c. 30° C./min.

Oxygen Content, wt.-%	Density * after Heat-Treatment, g./c.c.		
	Compacting Pressure, tons/in. ²		
	10	20	30
0.11	7.3	8.1	7.8
0.20	8.1	8.1	7.4
0.53	7.9	8.0	8.1

* Means of concordant duplicates.

The densities of the sintered compacts are given in Table V (a) and (b). It will be seen that for compacts pressed at 20 tons/in.² the final density generally decreases with increase of initial oxygen content and steadily increases with increase of temperature of the 4 hr. isothermal

treatment, C. The two most intense heat-treatments (A, and C, 880° C., Table V (a)) lead to densities of 8.4–8.6 in the lower-oxygen compacts, corresponding to porosities of only about 5 vol.-%.

The volume shrinkage of compacts may be estimated from a knowledge of initial density, initial oxygen content, and final density; it may also, of course, be calculated from initial and final micrometer measurements (diameter as well as length must be measured, since the radial shrinkage is less than the length shrinkage). Such calculations for a number of typical compacts result in very fair agreement, which gives confidence in the various measurements and assumptions made.

2. Heating in Argon, Nitrogen, and Carbon Monoxide Atmospheres.

Compacts of powders containing 0.11, 0.20, and 0.53 wt.-% of oxygen, pressed at 20 tons/in.², were heated in argon at 755° C. for 4 hr., being taken up to temperature at the rate of 20° C./min. Dilation curves obtained during the temperature rise and isothermally are shown in Fig. 18 (a) and (b), with the comparative results for treatment in a hydrogen atmosphere. It will be seen that the curves obtained during the rise of temperature in an argon atmosphere are initially similar to those obtained during heating in hydrogen, but that none of them shows the characteristic extra expansion found at somewhat higher temperatures in hydrogen. This is some confirmation that the extra expansion is indeed due to inflation by steam, as suggested above. During the isothermal treatment at 755° C., compacts heated in argon are seen to have shrunk further than those heated in hydrogen after a given time, undoubtedly owing to their smaller previous expansion. The shrinkage rates are, however, comparable, and show that shrinkage due to reduction is much less important than shrinkage due to sintering, for compacts having oxygen contents up to 0.53 wt.-%.

Experiments in a nitrogen atmosphere gave dilatometric results almost identical with those found in argon. Experiments in carbon monoxide, on the other hand, showed expansions during the latter part of the temperature rise even greater than those found in hydrogen (Fig. 19). It is likely that the carbon dioxide formed during the early stages of reduction becomes strongly chemisorbed, probably as the carbonate ion, on the unreduced oxide;³⁰ then during the latter part of the temperature rise, this gas is desorbed (or the carbonate ion decomposed), so that the inflation of the compact is at this stage especially rapid and marked.

In several heat-treatments carried out in the non-reducing atmospheres, argon and nitrogen, a red deposit was found in cooler parts of the dilatometer tube. Chemical tests and electron-diffraction photo-

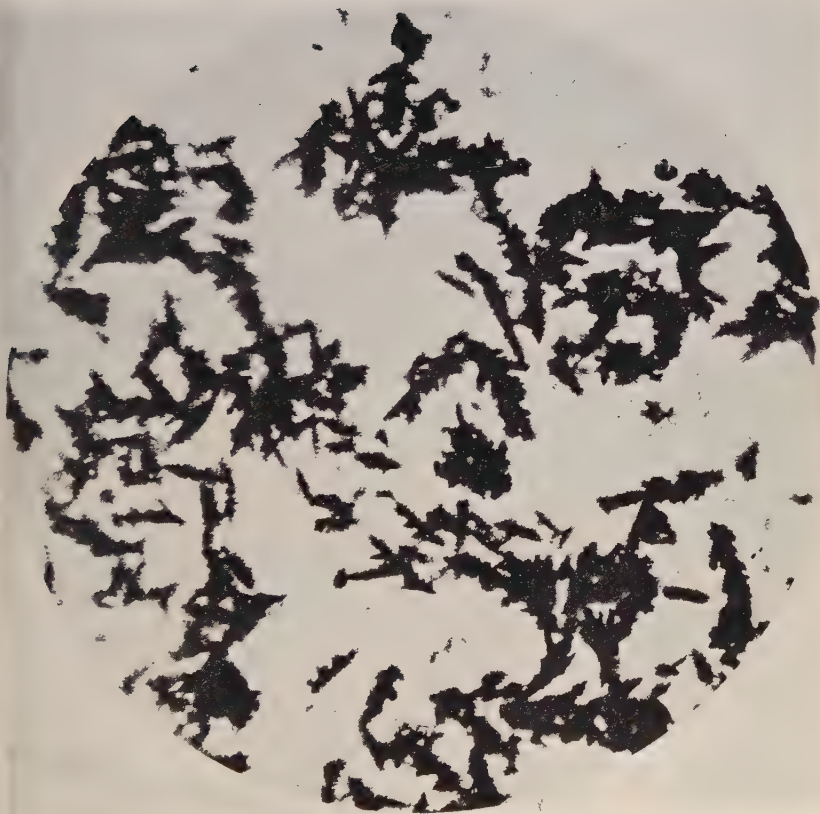


FIG. 23.—Copper Powder. $\times 200$. Transmitted Light.

[To face p. 380.]



FIG. 24.—Deoxidized Rim of Compact Heated in Argon.
Unetched. $\times 150$.

graphs showed it to be cuprous oxide. The compacts in question lost weight; the percentage loss was greater than their oxygen content but less than their cuprous oxide content, as shown in Table VI.

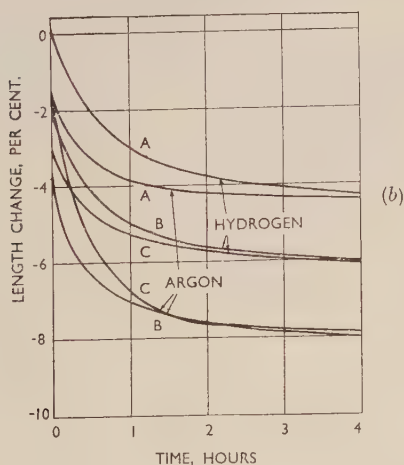
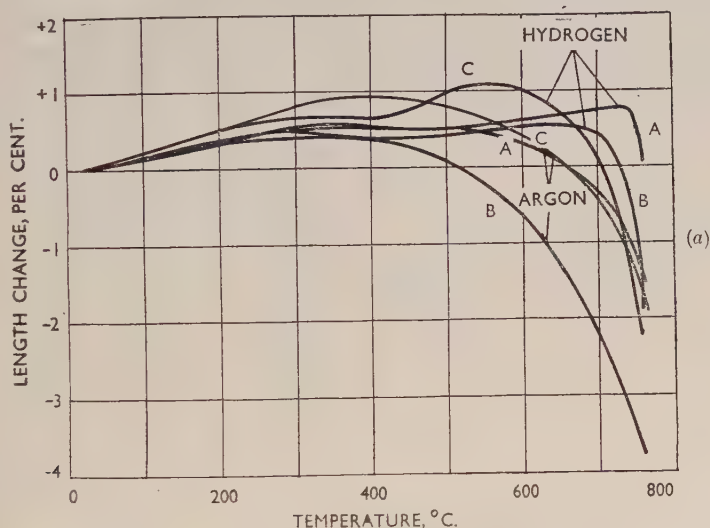


FIG. 18.—Comparison of Heat-Treatments in Argon and Hydrogen. (a) Length Changes during Temperature Rise. Heating rate: 20°C./min. (b) Length Changes during Isothermal Heat-Treatment at 755°C. Compacting pressure 20 tons/in.². Initial oxygen content: A 0.11, B 0.20, C 0.53 wt.-%.

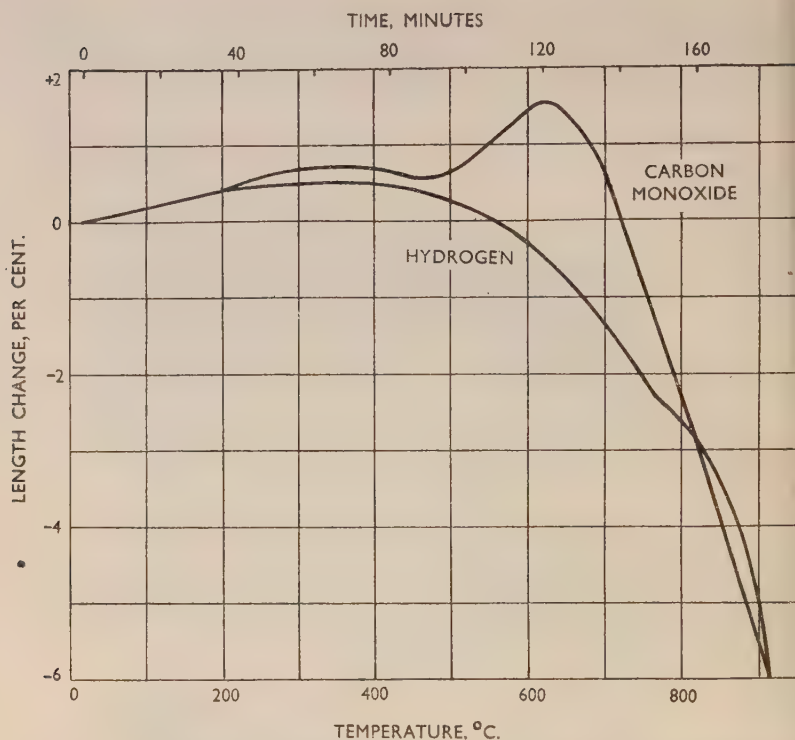


FIG. 19.—Comparison of Heat-Treatments in Carbon Monoxide and Hydrogen. Length Changes during Temperature Rise. Heating rate: 5°C./min. Initial oxygen content: 0.53 wt.-%. Compacting pressure: 20 tons/in.².

TABLE VI.—Comparison of Weight Loss during Sintering in Argon, with Oxygen and Oxide Contents.

Compacts pressed at 20 tons/in.², heated to 755°C. at 20°C./min. , held there for 4 hr., cooled to 20°C. at *c.* 30°C./min.

Oxygen Content, wt.-%	Cuprous Oxide Content, wt.-%	Weight Loss during Sintering, %	Percentage of Cuprous Oxide Volatilized	
			From Weight Loss	From Microphotograph
0.11	0.98	0.13	13	...
0.20	1.79	0.34	19	...
0.53	4.73	1.07	23	28

Furthermore, micro-examination showed considerable spheroidized cuprous oxide in the interior of the compacts, but none in the rim (see

Fig. 24, Plate XLVI). It is likely that in the absence of a reducing atmosphere, cuprous oxide volatilizes as such through pores in the surface layers of the compacts, doubtless until the pores close up in the sintering process. Such volatilization (at very low partial pressure) would leave the cuprous oxide content of the core of the compact substantially unaltered and would lead to a negligible oxide content of the rim, provided that it were rapid compared with the rate of solid diffusion of oxide. On this hypothesis, calculation from the depth of the deoxidized rim (in the case of the compact shown in Fig. 24) shows a percentage loss of cuprous oxide in good agreement with that deduced from the loss in weight (Table VI). The increase of the percentage loss of cuprous oxide as the initial oxygen content of the compacts is increased from 0.11 to 0.53 wt.-% is probably a consequence of the greater initial porosity associated with higher oxygen content (Table II).

III.—DISCUSSION.

1. Processes Leading to Dimensional Changes During Heat-Treatment.

The present results and general physical theory can be used to give a qualitative picture of the dimensional changes that occur in copper compacts during the complete sintering process, with particular reference to the influence of oxide. It is convenient to represent the various processes occurring during temperature rise schematically as in Fig. 20, where the thin (numbered) lines are hypothetical dilation/temperature curves for each separate process, and the thicker line, the algebraic sum of the hypothetical length changes at any temperature, is the observable dilation/temperature curve. The main features of the individual processes are as follows :

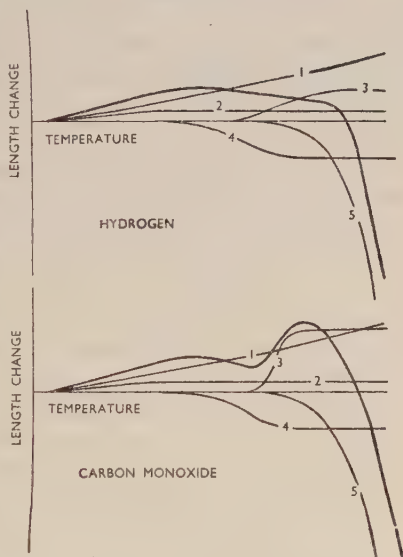


FIG. 20.—Schematic Representation of Length Changes during Heating, due to Various Processes.

KEY.

- (1) Solid thermal expansion.
- (2) Inflation caused by gas thermal expansion.
- (3) Inflation caused by gas production.
- (4) Shrinkage caused by reduction.
- (5) Shrinkage caused by sintering.

(a) Solid Thermal Expansion (Curve 1).

This, of course, begins at the start of the heating process, and increases approximately rectilinearly with increase of temperature. Its magnitude decreases with increase of oxide content of the compact, but for the small oxide contents of practical powders it is not likely to be significantly less than that of pure copper. Unlike all the other changes to be discussed, solid thermal expansion is instantaneous and thermally reversible, so that it is unaffected by heating rate and has no influence on the dimensions of the final cooled compact.

(b) Inflation Caused by Gas Thermal Expansion (Curve 2).

This begins as soon as the excess gas pressure in closed or partly closed voids, due to rise of temperature, becomes large enough to produce metal movement either by frictional slip of unsintered particles over one another (with rupture of cold-welded areas) or by plastic deformation of firmly anchored particles; as the temperature rises, the former movement becomes less easy owing to the anchoring action of sintering, while the latter becomes easier owing to the fall in yield point. High heating rates favour the inflation, because gas in partly closed voids has less time to escape and thus reaches a higher pressure. Oxide in the compact indirectly influences the inflation in three ways: (i) by its influence on total porosity (Part A), increase of which leads to greater possible inflation; (ii) by its probable influence in decreasing the percentage of *closed* pores, and consequently in assisting gas escape; (iii) by its influence in decreasing cold welding in the green compact. The net effect produced by oxide on the inflation is greatest in the range of oxide contents up to about 3 wt.-% (Fig. 12). It is likely that, after some inflation due to gas thermal expansion has occurred, leakage due to bursting of many of the closed pores stops the process before much sintering has started.

(c) Inflation Caused by Gas Production (Curve 3).

This occurs only in reducing atmospheres that produce gases (steam or carbon dioxide) which for physical or chemical reasons can leak from partly closed pores less readily than the gases (hydrogen or carbon monoxide) from which they are produced can diffuse in. It begins shortly after the onset of reduction, when sufficient gas pressure has been built up. It is not marked for low-oxygen or high-oxygen compacts heated in hydrogen, owing probably to the small amount of steam available in the former case and to the small amount of closed porosity in the latter; it can, however, be high for low-oxygen (0.53 wt.-%) compacts heated in carbon monoxide, probably because the moderate

amount of carbon dioxide produced is held by chemisorption within the compact until temperatures are reached at which the pores have begun to close by sintering, whereupon its desorption into closed pores produces a large inflationary pressure. Similarly, if an oxide film becomes sealed in owing to the formation of a metal film on its surface, as discussed in the section on heat-treatment in hydrogen, subsequent diffusion of hydrogen to it through the metal can produce a marked inflation that may temporarily slow down the net shrinkage.

(d) *Shrinkage Caused by Reduction (Curve 4).*

This probably begins at quite low temperatures, around 225° C., but does not become rapid until perhaps 500° C. It naturally increases with increase of initial oxide content, but is small for the low-oxygen (<1.0%) powders of practical importance.

Although reduction shrinkage does not, of course, occur in argon or nitrogen atmospheres, the loss of oxide by volatilization that then occurs probably leads to at least as great a shrinkage.

(e) *Shrinkage Caused by Sintering (Curve 5).*

This again may begin at low temperatures, as the tendency of mildly heated copper powder to "stick" indicates, but it certainly does not become extensive until at least 500°–600° C. Very rapid shrinkage then sets in, the rate being maintained if the temperature rise is continued, but markedly diminishing with time under isothermal conditions. There seems little doubt that the initial rapid shrinkage is caused by the progressive collapse, by plastic deformation due to the surface forces, of open pores from which gas can readily escape; and thus increase of initial oxygen content from 0.11 to 0.53 wt.-%, which leads to a considerable increase in green porosity (Table II), causes sintering shrinkage to become apparent sooner (Figs. 10, 11). The mechanism of sintering shrinkage, including the very slow ultimate shrinkage not shown in Curve 5 of Fig. 20, is further discussed below.

It is quite clear that the actual form of the dilation/temperature curve obtained can be greatly modified by relatively minor changes in the incidence and extent of the five component processes just discussed. The early expansive stages of the heat-treatment are greatly influenced by the amount and type of porosity in the green compacts, and the extent and ease of the oxide-reduction process, which are determined for any particular powder by its oxide content and the compacting pressure. The large rapid shrinkage due to sintering is influenced by porosity mainly in that the more porous green compacts have the further to

shrink; and the amount of oxide present (when reduction shrinkage is ignored) appears usually to produce little other effect, perhaps because it is totally reduced before much sintering has begun, or (in the case of neutral-atmosphere sintering) because at sintering temperatures it is mechanically weak and also appreciably soluble in copper, so that it is easily and incidentally balled-up either by plastic deformation or by diffusion induced by the surface forces. Thus, it appears that electrolytic copper compacts pressed at 20 tons/in.², having initial oxygen contents of 0.11, 0.20, and 0.53%, can—despite their widely different initial porosities—readily be sintered to a density of *c.* 8.5, independent of initial oxide content; this is a matter of some practical importance.

The present values for green density and overall shrinkage of the 0.20% oxygen compacts agree quantitatively, so far as they overlap, with some results obtained by Cook and Pugh²¹ using an electrolytic powder similar to the present in size distribution, of which the (undetermined) oxygen content was probably 0.2–0.3%. Cook and Pugh pointed out that relatively dense sintered compacts are more readily obtained from electrolytic and chemically precipitated copper powders than from powders made by hydrogen reduction of the oxide. They found much smaller overall shrinkages (and, at high compacting pressures, considerable expansions) of compacts made from reduced powders, and the sintered compacts contained much closed porosity. They attributed these effects to the presence of adsorbed gases and unreduced oxide in the original powder, a view supported by the present work: evidently, dilatometric studies of such compacts would have much interest.

In the experiments of Cook and Pugh, the overall shrinkage of lightly pressed compacts of the reduced powders, and the overall expansion of heavily pressed compacts, were found to increase with decrease of particle size. Now a reduced powder of small particle size may be expected to carry *more* superficial oxide (formed by air exposure), but *less* unreduced internal oxide, than one of large particle size. Thus, the reduction shrinkage of its lightly pressed, initially porous, compacts will be larger than that of similar compacts made from powder of larger particle size: while the inflation of its heavily pressed compacts, in which superficial as well as internal oxide is likely to be sealed in, will also be larger than that of similar compacts made from powder of larger particle size if this carries less total oxide.

2. The Mechanism of Sintering.

The present experiments have only indirect bearing on the mechanism of sintering, but they prompt certain suggestions. There is ample

evidence that the sintering process involves: (a) rapid collapse of open pores, with expulsion of gas, (b) spheroidization of pores, (c) slow disappearance of closed pores. Mackenzie and Shuttleworth¹² believe that the rapid process must occur by plastic deformation under the surface stresses, with surface and volume diffusion playing the minor role of restoring evenness to the deformed surfaces. They point out that such a process should also proceed at a closed pore until it has shrunk so that the pressure of the retained gas inside it balances its surface stress according to the well-known bubble equation, $p = \frac{2\sigma}{r}$.

Rhines, Birchenall, and Hughes¹¹ have attempted to explain the eventual disappearance of closed pores by supposing vacant lattice sites to diffuse from them to the compact surface. This tacitly assumes that the closed pores are free of gas, and if this unlikely contingency were indeed the case, there is no reason why they should not disappear as rapidly as open pores, e.g. by plastic deformation. It is much more likely that the slow disappearance of closed pores is governed by the diffusion of compressed gas from them through the lattice to the compact surface or to still-open pores or rifts. The gas particles concerned, in hydrogen sintering, are H, H₂, H₂O, and N₂; the first can doubtless diffuse interstitially, and the others are by no means too large to diffuse with the help of vacant lattice sites. Even CO and CO₂, concerned in carbon-monoxide sintering, might slowly escape from the pores by such lattice diffusion under a pressure gradient.* In the present work, the latter parts of the isothermal shrinkage curves may be seen (Figs. 15, 18 (b)) to indicate a slow shrinkage not much influenced by initial oxygen content or compacting pressure, and having a small temperature coefficient, such as would be expected if the shrinkage is here limited by gas diffusion from closed pores.

SUMMARIZED CONCLUSIONS.

The following summarized conclusions drawn from the present work naturally refer to compacts made from variously oxidized *electrolytic* copper powder only.

(1) The porosity of green compacts decreases with increase of compacting pressure from 10 to 30 tons/in.², and varies in a complex manner with oxygen content.

(2) The specific volume of green compacts increases with increase of oxygen content.

* The welding-up of pores containing these gases during the hot rolling of rimming steel is well known, and may be dependent upon gas escape by lattice diffusion.

(3) There is a hump in the green porosity/oxygen content and green specific volume/oxygen content curves in the composition range 0.1–3 wt.-% oxygen; it is maximal at 1%. It is probably caused by the surface oxide on the particles having maximal resistance to penetration or fragmentation during pressing when its thickness corresponds to this composition.

(4) During heat-treatment in reducing atmospheres, the compact length at first increases, owing to solid thermal expansion, inflation due to expansion of trapped gas, and inflation due to gases produced by oxide reduction. The inflation is maximal for compacts having oxygen contents of 1–2 wt.-%.

(5) Shrinkage, due to oxide reduction and/or metal sintering, sets in at c. 600° C. It is at first rapid and finally very slow, although still observable in compacts heated for 4 hr. at 880° C.; this ultimate shrinkage is probably limited by the rate of diffusion of trapped gases from closed pores.

(6) Oxide reduction is substantially complete after compacts have been heated in hydrogen for 4 hr. at 435° C. or higher.

(7) Oxide volatilizes from the outer layers of compacts heated for 4 hr. at 755° C. in argon or nitrogen.

(8) Compacts of sintered density c. 8.5 are obtained by heating at 950° C. for 1 hr. or 880° C. for 4 hr., if the initial oxygen content is not more than c. 0.5 wt.-%. For higher initial oxygen contents the sintered density decreases, to 7.8 for an initial oxygen content of 11.2% (cuprous oxide).

(9) The results are in harmony with current general theories of sintering.

ACKNOWLEDGEMENTS.

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APPENDIX I.—Capillary Flowmeter.

The design of this apparatus, used to measure the rate of flow of gas into the differential dilatometer, is based on that of Pourbaix.²⁷ The gas passes into a small reservoir and through a capillary tube (Fig. 21) whence it is led into the dilatometer. The pressure difference created between the two ends of the capillary is measured by means of the butyl phthalate manometer, and is used after calibration to determine the rate of flow of gas through the apparatus. Four interchangeable capillaries of 0.1, 0.2, 0.3, and 0.4 mm. dia. allow any desired range of rate of flow to be measured with an accuracy of $\pm 5\%$ or better.

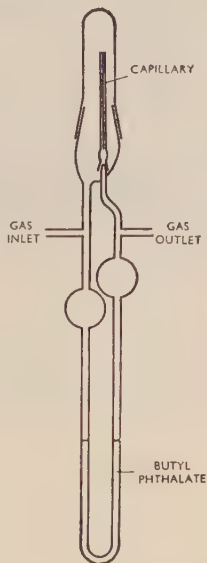


FIG. 21.—Capillary
Flowmeter.

Combining equations (1) and (2) :

$$2D = \frac{x \cdot AB}{l_{20}^p(\Delta_p - \Delta_{\text{SiO}_2})} = \frac{yBC}{l_{20}^c(\Delta_p - \Delta_c)}$$

$$\therefore \Delta_p - \Delta_c = \frac{y}{x} \cdot \frac{BC}{AB} \cdot \frac{l_{20}^p}{l_{20}^c} \cdot (\Delta_p - \Delta_{\text{SiO}_2})$$

and
$$\Delta_c = \Delta_p - \frac{y}{x} \cdot \frac{BC}{AB} \cdot \frac{l_{20}^p}{l_{20}^c} \cdot (\Delta_p - \Delta_{\text{SiO}_2}) \quad . \quad . \quad . \quad (3)$$

The length change of the compact is given as a percentage of the original length by $100 \cdot \Delta_c$ and may thus be obtained at any temperature by measuring the value of y at the x value for that temperature from the dilatometer record, and substituting this value and the appropriate constants into equation (3). (A slight correction is necessary if the original temperature is other than 20°C .)

SHEARING OF METAL BLANKS.*

1284

By T. M. CHANG,† Ph.D., B.Sc. (Eng.).

SYNOPSIS.

The results are given of investigations on the effects of clearance, tool shear, and tool curvature in the shearing of circular blanks. The materials tested included cast iron, mild steel, brass, copper, zinc, aluminium, and lead, ranging in thickness from 0.036 to 0.500 in. The tools employed had dia. of 1.6 in., clearances up to 58% of the thickness of the material, and shears to as much as 356%.

Altogether four separate sets of apparatus and recording systems were used, and the results show: (i) that the basic modes of fracture in blanking are essentially the same as those in bar shearing described in a previous paper (*J. Inst. Metals*, 1950-51, 78, 119); (ii) that the provision of an optimum clearance on the tool has the desirable effect of reducing both the maximum blanking load and the shearing work, the optimum clearances recommended being as follows: cast iron, 5-10%; mild steel, 5-10%; brass (70:30), 0-10%; copper, 0-10%; zinc, 0-5%; aluminium, 0-5%; lead, 0; and finally (iii) that the characteristics of tool shear can be derived from those of a flat punch by a graphical construction.

ALTHOUGH the blanking of sheet metal has been a common commercial practice for a number of years, there appears to have been no comprehensive investigation of the mechanism of this operation. Consequently, even such important factors as the optimum clearance and shear to be used with different metals under various conditions are still matters of controversy, and the sheet-metal workers are more often guided by practical experience than by accurate scientific knowledge. It has been the purpose of this research to obtain some reliable data concerning the types of shear fracture and the effects of clearance, curvature, and shear on tools, which might be of use in the sheet-metal industry.

I.—EXPERIMENTAL.

1. Apparatus for $\frac{1}{2}$ -in.-Thick Blanks.

The apparatus is shown in Fig. 1. It was designed to blank holes of 4, 2.5, and 1 in. dia. from a circular specimen 8 in. in dia. It will be seen that the apparatus consists of a base plate (*A*) and a cover (*C*), which are both spigotted to the body (*B*). A hole is drilled through the centre of the base plate to facilitate the ejection of the sheared blanks. In the cover, a hole 4 in. in dia. is bored through the middle to guide the 4-in. punch and also to house the sleeve (*F*) for the 2.5-

* Manuscript received 18 July 1950.

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and 1-in. punches. The die ring (G) rests on the base plate and serves to locate the 1 and 2.5 in. die rings (H for the 1 in. die). In the illustration the apparatus is ready to punch the 1-in. hole. By taking out the sleeve (F) and the inner die ring (H), and replacing them by the 2.5-in. sleeve and die ring, the apparatus can be used to punch a 2.5-in. hole from the same blank; while with no sleeve or inner die ring, the same apparatus may be used to blank the 4-in. hole. The punches and dies are of Firth die steel hardened and ground, the base plate and cover of

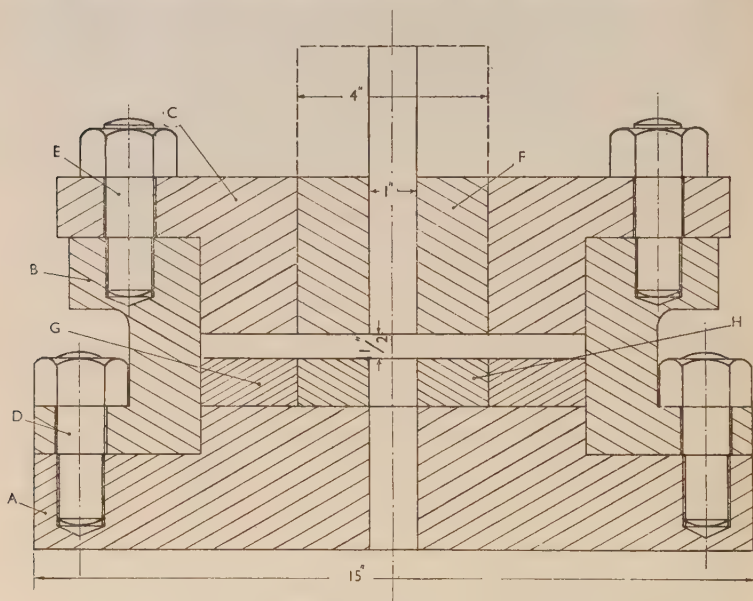


FIG. 1.—Apparatus for Blanking $\frac{1}{2}$ -in.-Thick Specimens.

cast iron, the sleeves and studs of mild steel, and the body is machined from forged steel.

The apparatus was placed in a 200-ton Amsler machine. The load was read from the dial on the machine, while the penetration of the punch was registered by a 0.001-in. dial gauge mounted on a mild-steel block placed directly on top of the punch. The clearances investigated with this apparatus are 0, 5, 10, and 20% of the metal thickness.

2. Apparatus for Materials 0.036, 0.080, and 0.130 in. Thick.

(a) The 6-in.-dia. Tool.

This was designed for shearing 6-in.-dia. blanks from specimens 9 in. in diameter. It will be seen from Fig. 2 that the main body (C) has a

raised central portion fitted with a hardened steel bush (*L*) to guide the spigot (*T*) of the punch (*A*). The cover (*H*) is fixed to the body by studs (*K*), and the die ring (*B*) is a good sliding fit in the body. The blank is the thick solid line on top of the die, and the ring on top of the blank is the blank-holder (*D*). The blank-holding pressure is provided by the four leaf springs (*E*), with the clamping-down ring (*F*) and the set screws (*M*) through the cover. The punch (*A*) is fitted with a hardened ring (*I*) which forms the actual cutting edge, and the dead weight of the punch is carried by the spring in the lower spigot. At the upper end

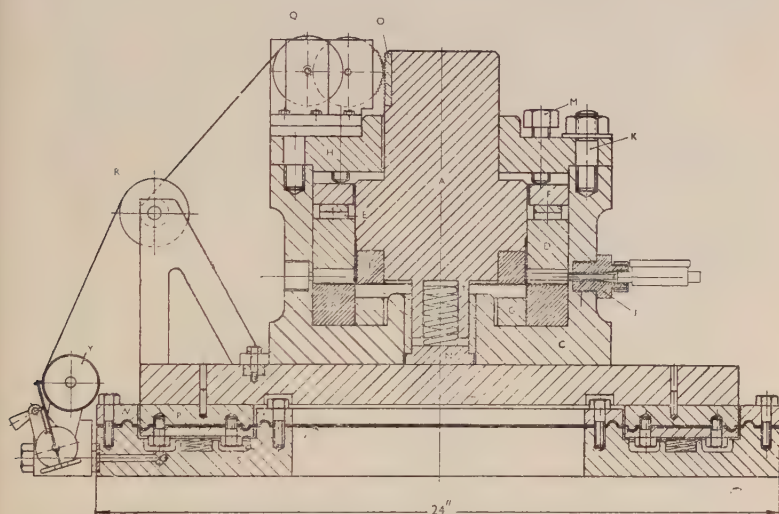


FIG. 2.—Blank Shearing Tool and Autographic Recorder.

of the punch, a brass rack (*O*) operates a system of gears and pulleys (*Q* and *R*) that magnifies the travel of the punch and finally actuates the drum of an ordinary engine indicator (*Y*). Four dial gauges, 90° from one another, are fixed by brass bushes (*J*) to the body and are used to measure the clearance and concentricity between the punch and die when the apparatus is assembled. Finally, the ring (*G*) inside the die is used for knocking out the sheared blank by means of two screws through the bottom of the body.

The surface of the die was kept flat and its diameter constant throughout the experiments, while clearances and shears were ground on to the punch. Altogether seven different clearances and five different shears were investigated, as can be seen in Table I. Here the clearance is the radial distance between the cutting edges of the punch and die, i.e. half

the difference between the diameter of the punch and die ; while the shear is the inclination between the cutting edges of the punch and die as shown in the inset to Fig. 11 (p. 407).

TABLE I.—*Clearances and Shears Investigated with the 6-in. Tool.*

Punch No.	Clearance :		Shear :		
	In.	% on 0.036 in. Material	In.	Degree on Radius (θ)	% on 0.036 in. Material
1	0	0	0	0	0
2			0.032	0° 37'	89
3			0.064	1° 14'	178
4			0.096	1° 51'	267
5			0.128	2° 27'	356
6	0.0026	7	0	0	0
7			0.032	0° 37'	89
8			0.064	1° 14'	178
9			0.096	1° 51'	267
10			0.128	2° 27'	356
11	0.0054	15	0	0	0
12			0.032	0° 37'	89
13			0.064	1° 14'	178
14			0.096	1° 15'	267
15			0.128	2° 27'	356
16	0.0075	21	0	0	0
17	0.0090	25			
18	0.0123	34			
19	0.0139	39			

In order to record the blanking load automatically during the experiment, the apparatus was placed on a pressure recorder, which was designed by Swift and Harland for use in the Engineering Laboratory of Sheffield University. In principle the recorder is merely a piston resting on a fluid housed in a cylinder. Any load applied to the piston is transmitted to the fluid, which in turn acts on an engine indicator that records the pressure autographically on sensitized paper. In the actual design of the recorder, the cylinder is an annular ring (*S* in Fig. 2) with a trough (*U*); whereas the piston (*P*) is made up of two circular rings with a piece of rubber diaphragm (*V*) between them. The diaphragm seals the fluid in the trough and is clamped firmly on to the cylinder by rings (*W*) and (*X*). The indicator (*Y*) is connected to the recorder base by a brass block, which also holds a screw pump to deliver fluid into the recorder. The area of the piston in contact with the fluid is exactly 224 in.², so that a pressure of 10 lb./in.² recorded by the indicator is equivalent to a load of 1 ton total on the recorder.

The experiments were carried out in a 200-ton hydraulic press specially designed for compression tests.

(b) *The 1-in.-dia. Tool.*

A cross-section of the tool and press employed is shown in Fig. 3. The press was originally designed by Swift for drawing and ironing

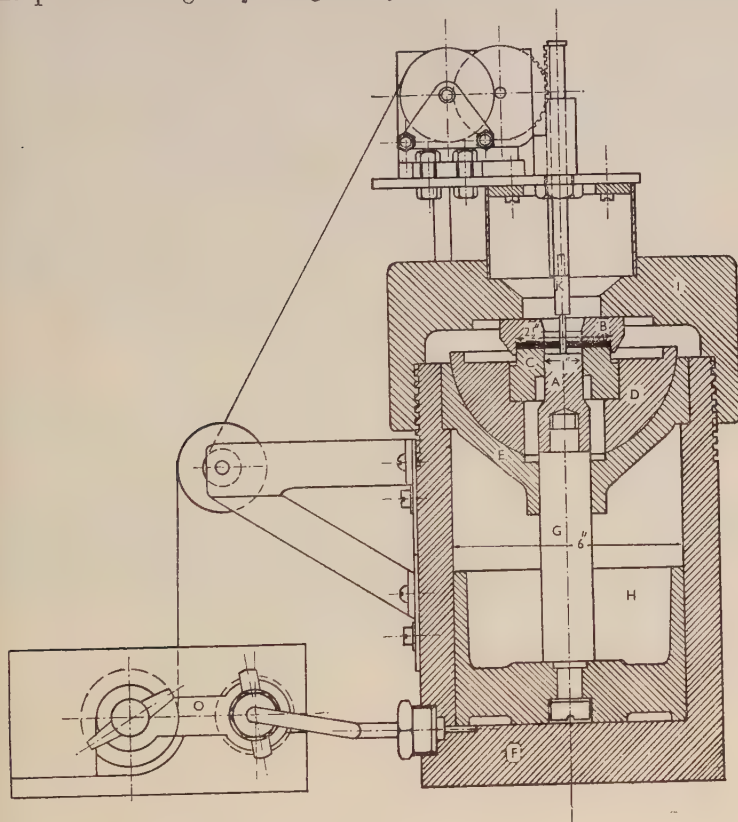


FIG. 3.—The Press Set Up for Punching with 1-in. Tool.

research in the University, and has already been described by him in detail.² The punching tool is composed of a punch (A), a guide-block (C), and a die (B). The punch (A) is screwed to the threaded spigot of the ram (G); while the guide-block (C) rests squarely in the hemispherical cup (D). The die (B) has a recess in its lower part, which is a close sliding fit on the upper part of the guide-block. Thus through the guide-block the die is brought to concentricity with the punch. The

specimen is placed in the recess of the die on top of the guide-block and is pressed firmly against the latter by screwing down the cylinder-head (*I*).

Practically the same recording system is employed here as in the case of the 6-in. tool. The movement of the punch is transmitted by a rack rod that passes through a central hole in the blank and rests directly on top of the punch. The pressure of the oil acting on the piston (*H*) and the indicator (*O*) is obtained from an accumulator.

Altogether 18 punches have been investigated, 17 of them being used for the investigation of clearance effects and one (with 0.064 in. shear and no clearance) for the shear effects. The clearances investigated range from 0 to 0.021 in., which is 58% on the 0.036-in. material, a range far beyond industrial practice.

(c) *The $\frac{1}{4}$ -in.-dia. Tool.*

This is shown in Fig. 4, which is self-explanatory. In order to obtain an autographic diagram for the experiment, the tool is placed in a 20-ton Amsler machine, and the travel of the crosshead of the machine is magnified by a system of pulleys. The tests cover almost the same range of clearances and shears as the 1-in. tool.

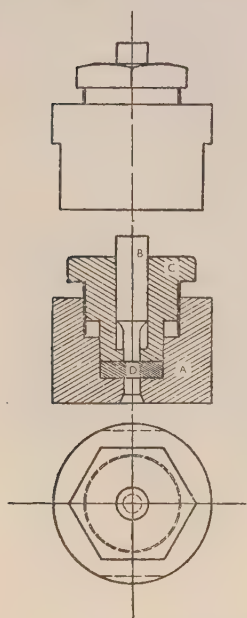


FIG. 4.—The $\frac{1}{4}$ -in. Punching Tool.

A = Die; B = Punch;
C = Guide-Block and
Blank-Holder; D = Blank.

3. Test Details and Materials Used.

For each experiment, at least two blanks were tested under identical conditions. If the two tests gave appreciable difference in the results, a third experiment was made.

Approximately 5–10 min. was the time allowed for each test on the $\frac{1}{2}$ -in.-thick material. For the thinner materials using self-recording devices, between $\frac{1}{2}$ and 1 min. was the time of each experiment.

Only mild steel and aluminium were tested with the apparatus shown in Fig. 1 and described on p. 393. For the other apparatus, the materials were supplied in sheets of 0.036–0.250 in. thickness. For cast iron, however, the specimens were machined from $\frac{3}{8}$ -in.-thick cast discs. The average thickness and mechanical properties of each material are shown in Table II.

TABLE II.—*Mechanical Properties of Blanking-Test Specimens.*

Material	Thickness, in.	Diamond Pyramid Hardness Number	Yield Point, tons/in.*	Nominal U.T.S., tons/in.*	Elong- ation, %	Reduction in Area, %	
						At max. load	At failure
Lead	0.130	4.2	...	0.91	76
	0.252	,,	...	0.89	88
Aluminium	0.500	23	...	4.9	...	33	89
	0.130	23	...	5.9	41
	0.080	24	...	5.5	42
	0.036	21	...	5.7	32
Zinc	0.130	61	...	9.8	31
Copper	0.130	64	...	15.0	48
Brass	0.130	77	...	22.4	51
	0.080	77	...	22.5	53
	0.036	83	...	22.6	43
Mild steel	0.500	146	17.3	30.5	...	21	61
	0.126	104	16.3	24.3	37
	0.080	99	16.3	24.5	38
	0.036	94	14.7	21.0	35
Cast iron	0.125	213	...	8.4

The specimens for the 6-in. tool were a little less than 9 in. in outside dia. with a central hole 2.75 in. in dia. to provide clearance for the lower spigot of the punch (see Fig. 2). The material cut out from the centre of these large specimens was machined down to 2.5 in. in outside dia. and used in the tests with the 1-in. tool. A central hole, $\frac{1}{4}$ in. in dia., was drilled through this specimen so as to allow the extension of the rack rod to pass through as described above. The specimens for the $\frac{1}{4}$ -in. tool were trepanned out of the same stock of materials.

II.—DISCUSSION OF RESULTS.

1. *The $\frac{1}{2}$ -in.-Thick Blanks.*

The results of these experiments are recorded in Table III. It will be seen that as the diameter of the tool increases, there is a systematic decrease in the nominal ultimate shearing stress with the exception of the 20% clearance. It appears, therefore, that within the limit of clearances used in industry, the shearing strength of materials is an inverse function of the tool diameter.

In order to compare the shearing characteristics obtained with tools of different diameters, the shearing stress/penetration curves are super-

TABLE III.—*Shearing-Test Results ($\frac{1}{2}$ -in.-Thick Blanks).*

Material	Clear- ance, %	Dia. of tool, in.	Max. Shearing Load, tons	Nominal Ult. Shearing Strength, tons/in. ²	Punch penetration, %		Work Done,		No. of Tests
					At max. load	At failure	in.-tons	in.-tons/ in. ² of area	
Mild Steel	nil	1	35.9	22.8	24.5	121	13.85	8.80	3
		2.5	88.9	22.6	22.4	110	29.78	7.60	3
		4	135.7	21.7	21.5	119	48.74	7.77	2
		Bar	31.4	20.9	16.1	19	2.10	1.40	2
	5	1	35.7	22.7	23.2	106	9.80	6.23	3
		2.5	85.9	21.9	22.3	98	22.10	5.63	3
		4	128.9	20.6	22.0	106	35.30	5.62	3
		Bar	30.5	20.3	17.3	18	2.29	1.53	2
	10	1	34.5	22.0	24.4	77	7.19	4.56	3
		2.5	79.6	20.3	25.1	74	16.70	4.27	3
		4	123.2	19.7	23.2	84	28.16	4.50	3
		Bar	29.9	19.9	18.9	23	2.49	1.66	2
	20	1	33.5	21.3	31.3	35	4.75	3.01	2
		2.5	73.2	18.7	26.7	33	9.70	2.48	2
		4	118.3	18.9	27.5	32	15.38	2.45	2
		Bar	30.1	20.1	25.7	29	3.38	2.25	2
Aluminium	nil	1	6.58	4.19	24.6	112	2.60	1.66	2
		2.5	15.90	4.03	45.0	128	7.60	1.94	2
		4	24.50	3.90	28.5	105	8.99	1.43	2
		Bar	5.73	3.82	30.0	102	2.08	1.38	1
	20	1	5.98	2.86	47.4	61	1.11	1.09	1
		2.5	13.62	3.47	53.0	90	4.60	1.18	1
		4	22.00	3.50	51.6	101	7.45	1.19	1
		Bar	5.68	3.78	55.0	74	1.86	1.23	1

imposed in Figs. 5 and 6 (Plate XLVII). It is apparent from Fig. 5 that the curve for the 1-in. tool occupies the highest and outermost position, enclosing the largest area, showing that the resistance of the material to shearing is greatest with this tool. The 2.5- and 4-in. tools give very similar curves, indicating that within these limits there is little change in the behaviour of the metal in the shearing process. In the case of the bar, however, the curves drop at all clearances quite abruptly after passing the maximum, and the enclosed area is the smallest of all. It is, therefore, clear that between the straight-edged and the 1-in.-dia. tools there exists a marked difference, the unmistakable trend being for the resistance of the metal to increase with the increase in the curvature of the tool.

The characteristic curves for aluminium are shown in Fig. 6. There is a substantial spread in the initial rising portion of the curves before the maximum load. It seems that in the early part of the operation, greater punch penetration is possible under the same blanking load with tools of larger dia. This trend is also found in the case of the 20% clearance.

The effect of tool curvature can be explained to a certain extent by

the nature of the fractured surface of the blanks. The photographs of sheared specimens of mild steel in Fig. 7 (a) (Plate XLVIII) show that as the curvature of the tool is increased, there is a tendency for the formation of more cracks. Each of the multiple cracks represents a process of tongue formation, and so causes a check in the fall of the shearing load. Hence as the diameter of the tool is reduced, more checks are experienced in the diminution of the shearing load. The strain work is therefore greater. That multiple cracks are formed when using circular tools, as against a single crack in the case of the bar, is probably due to the fact that in the shearing of the bar, the metal is much freer to move in all directions, since there are several free edges where the metal is able to spread.

A proof of this statement has been sought by blocking the ends of the mild steel bar to be sheared, thus preventing the bar from extending endwise. The load/penetration curve of this test proved to be very similar to the curves obtained from circular blanks shown in Fig. 5. The work done per square inch of shearing area in this case works out to be 6 in.-tons, as against only 1.4 in.-tons when the ends are free, thus bringing the value very much nearer to that given in Table III for the circular blanks. What is more significant, however, is the formation of multiple cracks in the material which gives only a single crack when the ends are free to extend.

The sheared edges of aluminium blanks at zero clearance are, in general, covered by a broad and continuous burnished band. There is no evidence of the formation of incipient cracks, thus confirming that the abortive cracks found at the edges of aluminium bars are only edge effects. Since the sheared surfaces of the specimens from the circular and straight-edged tools are on the whole very similar, the characteristic curves which they yield are, therefore, also very much alike.

The effects of clearance on the shearing of mild steel for the 2.5-in. tool are shown in Fig. 8. It will be seen that the introduction of initial bending and the reduction in the maximum shearing load are fairly marked; while the decrease in the strain work by clearance is also pronounced.

As regards the sheared fracture, Fig. 7 (b) (Plate XLVIII) shows that in the case of mild steel the 5% clearance has reduced the multiple cracks to a single crack; 10% clearance serves to reduce the size of the single tongue, and 20% clearance eliminates the tongue altogether, though at this large clearance the taper on the sheared surface is appreciable. The effects of clearance on the larger blanks are just the same as those for the 1-in. blank shown in Fig. 7 (b), and their fractured surfaces are therefore not shown here.

It is apparent that for the elimination of the tongue and the reduction of strain work in mild steel, slightly larger clearance is needed for circular tools than for bars; for whereas in the case of the bar the tongue disappears at 5% clearance, the tendency for tongue formation persists even up to 10% clearance in circular blanks.

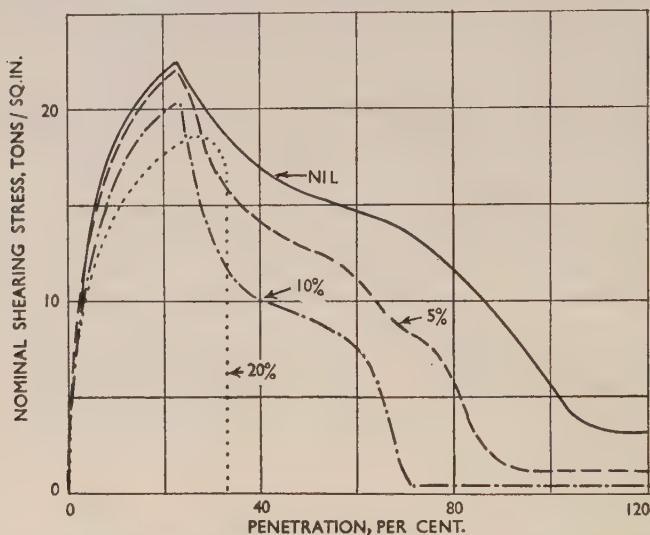


FIG. 8.—Effect of Clearance on Shearing Characteristics of 0.500-in. Mild Steel. (Diameter of die : 2.5 in. Clearance as indicated.)

2. *The Thinner Blanks.*

(a) *Effect of Clearance and Tool Curvature.*

Typical autographic diagrams from the three series of tests on mild steel, which have been replotted on the same scale, are shown in Fig. 9. It will be seen that the general shapes of the diagrams are very similar for the three sets of tools, showing that fundamentally the load/penetration characteristics of this material are not altered by a change in the curvature of the tool. It is to be noted, however, that with the 6-in. tool, the check in the fall of the blanking load is absent even at zero clearance, and that the blanking operation is complete at about 40–50% punch penetration. With the 1-in. tool, on the other hand, the fall in the load is still very gradual at 8% clearance, and at this clearance the load does not fall to zero until the punch has penetrated about 85% into the blank. This tendency for the more gradual fall in the blanking load is even more pronounced in the diagrams of the $\frac{1}{4}$ -in. tool. Here

none of the curves reach the horizontal ending of pure frictional load before the punch has penetrated 90% into the blank. This apparent effect of tool curvature may again be due to the reduction in the freedom for metal flow as the punch diameter is reduced. As a matter of fact, the blank punched by the $\frac{1}{4}$ -in. tool at zero clearance has a sheared edge (Fig. 7 (c), Plate XLVIII) very similar to that of the blank punched out of $\frac{1}{2}$ -in.-thick material with the 1-in. tool (Fig. 7 (b), nil clearance); both exhibit the formation of multiple cracks.

As the 1-in.-dia. punch blanking the $\frac{1}{2}$ -in.-thick material is geometrically similar to the $\frac{1}{4}$ -in. punch shearing the $\frac{1}{8}$ -in.-thick blank, the resemblance in the sheared edges mentioned above suggested that the shearing characteristics of geometrically similar combinations of tool and blank might be alike. This, however, is not found to be generally true. Table IV gives the results for mild steel obtained from four such combinations. It will be seen that as far as the shearing strength, S_s , is concerned, the agreement is good for each clearance, although the results from the $\frac{1}{4}$ -in.-dia. tool are a little higher than those of the others. The punch penetration at maximum load shows a general increase with decrease in diameter of the tool, but the punch penetration at failure of the blank

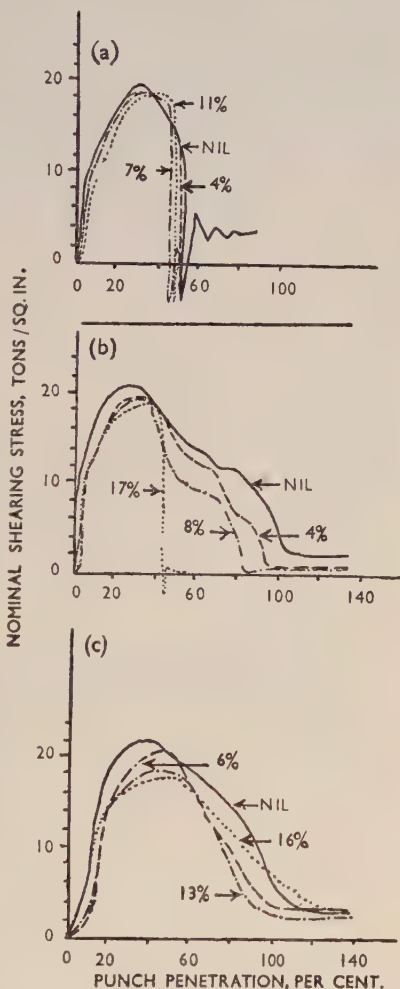


FIG. 9.—Autographic Diagrams for 0-126 in. Mild Steel. (Diameter of tool: (a) 6 in.; (b) 1 in.; (c) 0.250 in. Clearance as indicated.)

does not seem to follow any particular trend. The work done per square inch of shearing area, W , decreases with reduction in the blank

thickness, but does not seem to bear any definite relationship to it. With regard to the sheared edges, multiple tongues are found on the 4-in.-dia. blank at zero clearance, but only a single tongue is formed with the 5 and 10% clearances. For the 2½-in.-dia. blank, two prominent tongues are found at zero clearance, and a single tongue at 5 and 10% clearances. For the 1-in.-dia. blank, there is only a single tongue for all the three clearances tested; while no sign of any tongue formation is visible at the edges of the ¼-in. blanks at all clearances.

TABLE IV.—*Blanking-Test Results on Mild Steel with Geometrically Similar Combinations of Tools and Blanks.*

d	t	t/d	S_s			P			W		
			Clearance, %								
			0	5	10	0	5	10	0	5	10
4	0.500	$\frac{1}{4}$	21.6	20.6	19.7	21.5 (119)	22.0 (106)	23.2 (84)	7.77	5.62	4.50
$2\frac{1}{2}$	0.312	$\frac{1}{2}$	21.8	20.9	20.5	21.9 (100)	22.4 (79)	25.6 (30)	4.00	3.25	1.54
1	0.126	$\frac{1}{8}$	21.5	19.5	19.1	29.0 (98)	30.2 (89)	32.5 (73)	1.85	1.45	1.08
$\frac{1}{2}$	0.036	1.44	23.5	22.0	21.0	72.0 (144)	75.0 (167)	115.0 (200)	0.68	0.72	0.75

d = dia. of punch, in.

t = thickness of blank, in.

S_u = nominal ultimate shearing stress, tons/in.².

P = punch penetration, % : figures in brackets are the punch penetrations at failure of the blank; those without brackets are the punch penetrations at max. load.

W = work done per square inch of shearing area, in.-tons.

For the rest of the materials investigated, lead and aluminium give diagrams of flat tops and very gradual falls in the blanking load. Copper behaves in very much the same way as brass, showing a pronounced increase in punch penetration at failure with increase in tool curvature; while the diagrams for zinc and cast iron are typified by a sharp fall after passing the point of maximum load. On the whole, the curvature and clearance effects seem to be least in the case of zinc, and the sheared edges of cast iron and zinc alike have typical fractured surfaces for all clearances, with hardly any sign of a burnished band.

To sum up the information obtained from the autographic diagrams, curves such as those in Fig. 10 can be drawn to show the effects of clearance and tool curvature on the shearing strength of different materials and on the work done per unit shearing area to effect separation of the blank.

It is found from such curves that the shearing strength of most

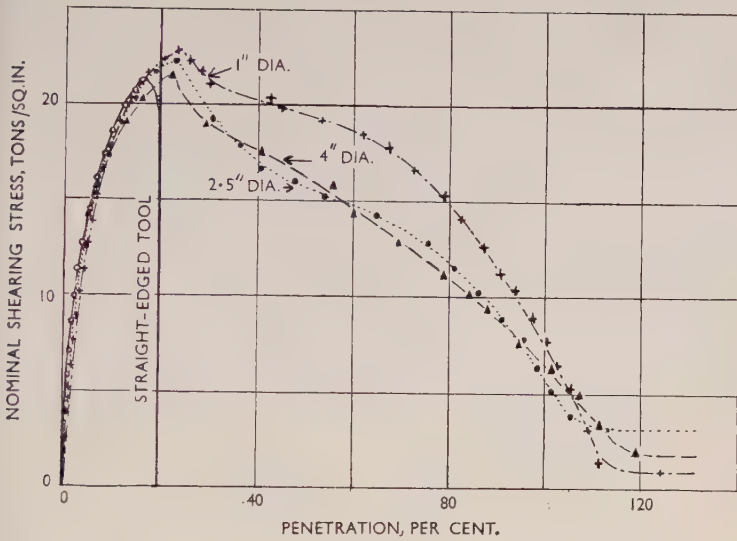


FIG. 5.—Effect of Tool Curvature on Shearing Characteristics of 0.5-in. Mild Steel. (Clearance : nil. Tool diameter as indicated.)

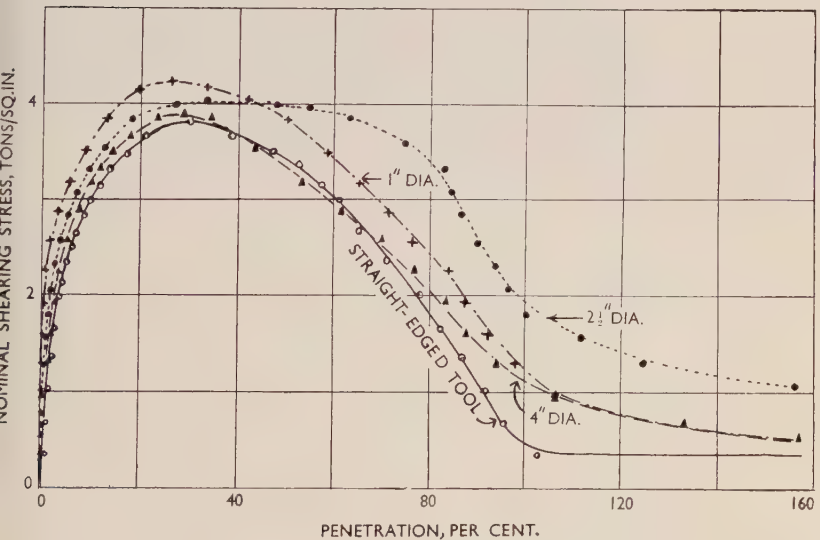


FIG. 6.—Effect of Tool Curvature on Shearing Characteristics of 0.5-in. Aluminium. (Clearance : nil. Tool diameter as indicated.)

BLANKING OF MILD STEEL

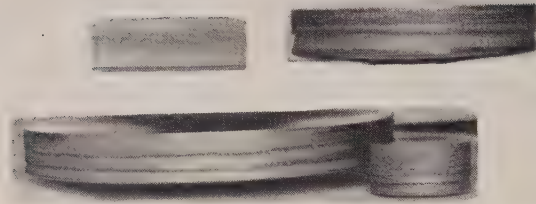


FIG. 7(a).—Sheared Specimens from Tools of Different Diameters.
(Thickness : 0.500 in.)

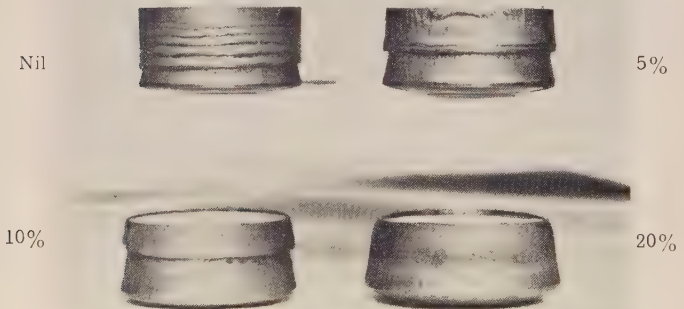


FIG. 7(b).—Elimination of Tongues by Clearance. (Clearance as indicated. Tool diameter : 1 in. Thickness : 0.500 in.)

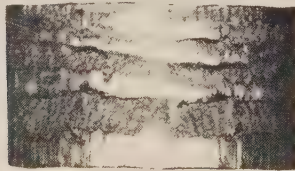


FIG. 7(c).—Sheared Edge of $\frac{1}{4}$ -in. Blank. (Clearance : nil. Thickness : 0.126 in.)

materials falls with increase of clearance, lead being a notable exception; that the fall in the ultimate shearing strength with clearance seems to be more rapid with the $\frac{1}{4}$ -in. tool; and that at small clearances the shearing resistance is smaller for tools of larger diameter.

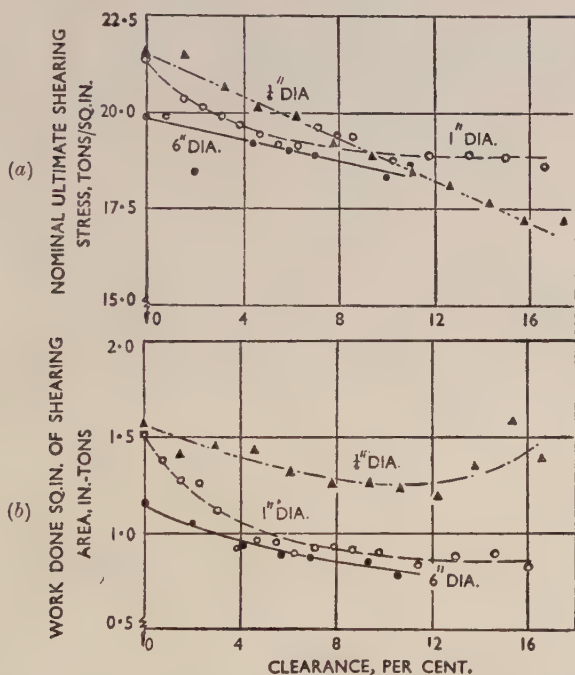


FIG. 10.—(a) Effect of Clearance and Tool Curvature on Ultimate Shearing Strength of 0.126-in. Mild Steel. (Tool diameter as indicated.) (b) Effect of Clearance and Tool Curvature on Work Done in Blanking of 0.130-in. Brass. (Tool diameter as indicated.)

It is interesting here to compare the values of the shearing strength with those of the nominal "ultimate tensile strength." Table V gives such a comparison and the ratios obtained. It will be seen that these ratios vary not only with different materials but also with tools of different diameter. This does not agree with the generally accepted view that the shearing strength of a material bears some definite ratio to its tensile strength.

The effect of increasing clearance on the work done in blanking is illustrated by Fig. 10 (b), which may be regarded as typical of all the metals tested. It will be seen that the work diminishes steadily up to clearances of about 10%, but remains steady or even shows a tendency

to rise at clearances greater than this. The specific work required also varies in an inverse manner with the tool diameter; this is probably due to the greater restriction to metal flow with tools of small diameter in proportion to the metal thickness.

TABLE V.—*Ratios Between Nominal Ultimate Shearing Stress and Tensile Stress.*

Material	Tensile, Stress, tons/in. ² t	Shearing Stress, tons/in. ² s_1 (6-in. tool)	Ratio, s_1/t	Shearing Stress, tons/in. ² s_2 (1-in. tool)	Ratio, s_2/t	Shearing Stress, tons/in. ² s_3 ($\frac{1}{8}$ -in. tool)	Ratio, s_3/t
Lead :							
0.130 in.	0.91	0.428	0.47	1.32	1.46	0.610	0.67
0.252 in.	0.89	0.525	0.59	1.03	1.15	0.635	0.72
Aluminium :							
0.130 in.	5.9	3.84	0.66	4.70	0.80	4.30	0.73
0.080 in.	5.5	3.90	0.71	5.04	0.92	4.10	0.74
0.036 in.	5.7	3.40	0.60	5.80	1.02	4.45	0.78
Zinc :							
0.130 in.	9.8	7.8	0.80	9.7	0.99	8.4	0.86
Copper :							
0.130 in.	15.0	10.6	0.71	11.6	0.77	10.5	0.70
Brass (70 : 30) :							
0.130 in.	22.4	15.8	0.71	16.9	0.75	17.4	0.78
0.080 in.	22.5	16.2	0.72	17.2	0.77	17.8	0.79
0.036 in.	22.6	17.0	0.75	18.6	0.82	18.9	0.84
Mild Steel :							
0.126 in.	24.3	19.9	0.82	21.4	0.88	21.5	0.88
0.080 in.	23.5	21.1	0.90	22.6	0.96	23.8	1.02
0.036 in.	21.0	18.4	0.88	21.5	1.02	20.6	0.98
Cast Iron :							
0.125 in.	8.4	15.1	1.80	22.2	2.65	26.1	3.10

(b) *Effects of Shear.*

Fig. 11 shows typical autographic diagrams obtained from punches of different shears. The diagrams indicate that the following points are common to all materials :

(i) The maximum ordinates of the diagrams decrease systematically with the increase in shear, but the penetrations of the punch at maximum load and at failure increase with the increase in shear.

(ii) As the shear is increased, the initial rise of the curve to the point of maximum load becomes more gradual; the same is true with the fall of the curves from the maximum point.

Referring to the inset to Fig. 11, it is evident that when a punch with shear rests vertically on the blank, it is the two lowest points of the cutting edge (points *A*) that are actually in contact with the blank. Thus the punch penetration forming the abscissa of the autographic diagrams is in fact the penetration of these two lowest points of the cutting edge. Hence, as the shear is increased, a shorter length of the cutting edge is brought into the metal for the same penetration of the punch during the initial part of the operation. It follows, therefore, that the load is built up more gradually. The same applies to the

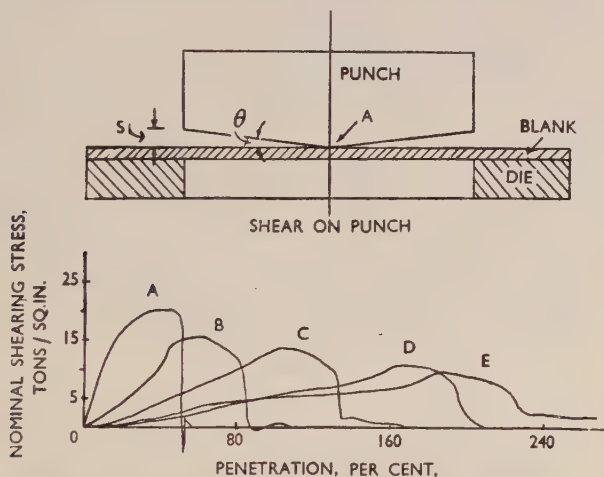


FIG. 11.—Effect of Tool Shear on 0.080-in. Mild Steel. (Clearance : nil. Tool diameter : 6 in. Shear : (A) nil ; (B) 0.032 in. ; (C) 0.064 in. ; (D) 0.096 in. ; (E) 0.128 in.)

failure of the blank; for with a punch of a greater shear, the cutting edge is brought more gradually into the zone of failure and so the fall of the curve becomes more gradual.

On the whole, the reduction in load with the increase in shear is almost linear for most materials. Within the range of shear investigated (356%), a reduction of 75% in the maximum blanking load has been recorded for the thinnest (0.036-in.) materials.

The increase in punch penetration at maximum load with the increase in shear is also not far from linear; while the effect of shear on work done seems to vary with different materials. Whereas cast iron, mild steel, and brass show an increase with increase in shear (Fig. 12) zinc has actually a tendency to decrease, and copper, aluminium, and lead seem to remain constant. The substantial increase with cast iron

is no doubt due to the delay in the fall of the shearing load as a result of the progressive nature of shearing by the sheared punch.

The shear effects with tools having certain clearances on them show practically the same trends as those found from the tools with no clearance.

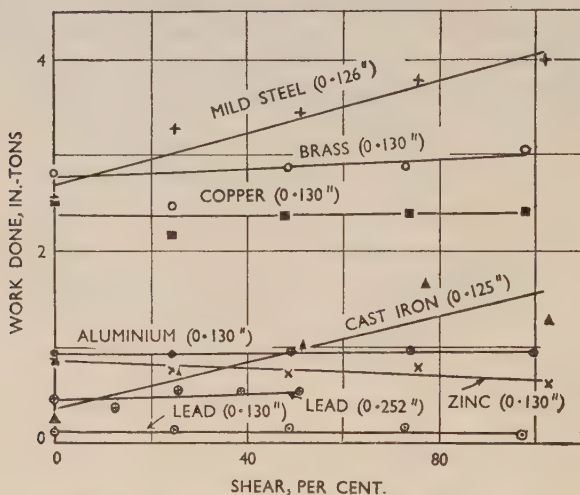


FIG. 12.—Effect of Shear on Work Done in Blanking. (Clearance : nil.)

III.—GRAPHICAL SOLUTION OF SHEAR CHARACTERISTICS.

Provided that the intrinsic shear-resistance of the metal at any section is dependent only on the local punch penetration, it should be possible to predict the punch load/penetration characteristic for a sheared punch of known profile from that for a flat punch. The procedure, which was suggested to the author by Professor Swift, is in effect a series of graphical integrations, and can best be explained by means of an example.

The inset to Fig. 13 shows a quadrant of a sheared punch with the profile of its cutting edge developed. It is easy to find that the equation of the profile of the cutting edge is :

$$y = S \cdot \sin \theta$$

where S = shear on the punch. Thus, if S is known, the profile of the cutting edge which is a sine curve can be plotted.

The following concrete example will serve to show the necessary procedure for the solution of the shear characteristics.

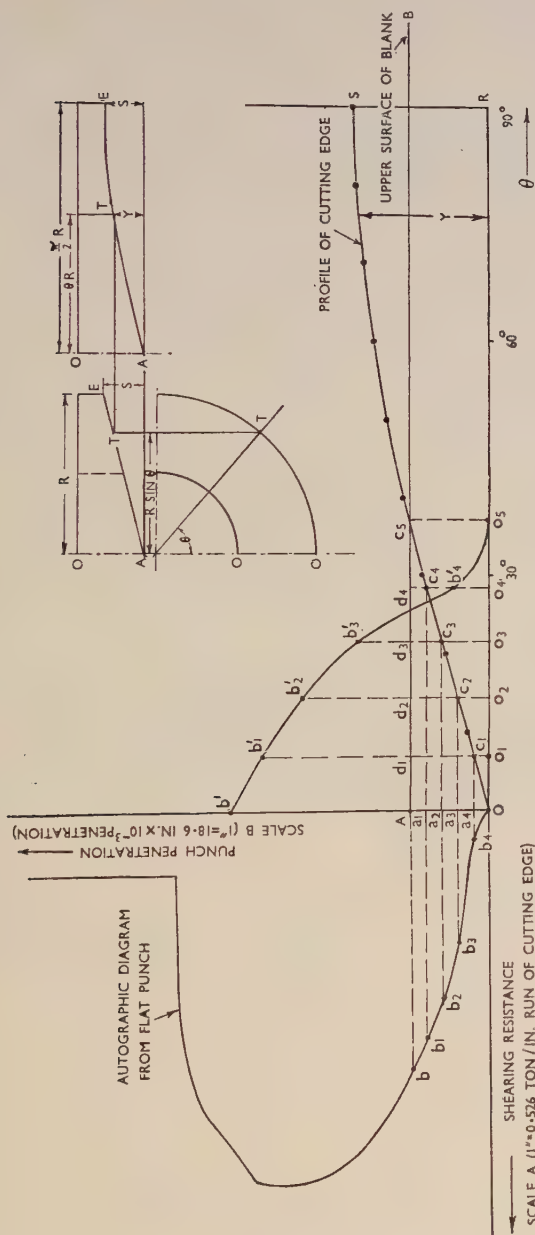


FIG. 13.—Graphical Solution of Shear Characteristics.

Given the autographic diagram of 0.126-in. mild steel, blank-sheared by a flat punch, it is required to find the load/penetration curve of the same punch with 0.032 in. shear, blanking the same material of the same thickness.

The first step is to magnify the given autographic diagram to a size convenient for graphical construction, with scale *A* showing the shearing-resistance in tons per inch run of the cutting edge, and scale *B* showing the punch penetration in inches (see Fig. 13).

At the right of the autographic diagram, the profile of a quadrant of the cutting edge of the sheared punch is plotted. This can easily be done, using the above formula, by substituting 0.032 in. for *S* and successive values of $10^\circ, 20^\circ, 30^\circ, \dots 90^\circ$ for θ . For the convenience of graphical construction, scale *B* is best used for plotting the values of y thus obtained; while 1 in. on the horizontal axis *OR* may be used to represent 10° of θ . The plotted profile is shown as *OS* in the figure, with *OR* as its projection on the horizontal axis, which is 9 in. in length.

Now let the punch penetrate into the blank a distance equal to *OA*. Then *AB* will be the upper surface of the blank, and *Oc₅* will be the section of the cutting edge actually in action, since the remaining parts of the cutting edge *c₅S* have not yet touched the blank. Obviously, the point *O* has penetrated deepest into the metal, and should, therefore, sustain the highest shearing-resistance; whereas, at point *c₅*, which is just on the surface of the blank, the resistance should be zero. Now, the shearing-resistance at *O*, which corresponds to the penetration *OA*, can readily be found from the autographic diagram by drawing a line *Ab* perpendicular to *OA* at *A*. Then the length *Ab* will obviously represent the shearing-resistance at *O*. If along the perpendicular *OA* a distance *Ob'* is marked off equal to $\frac{1}{2}Ab$, then *Ob'* will also represent the shearing-resistance at *O*.

At point *c₁* on the cutting edge, the penetration is *d₁c₁* ($= Oa_1$) and the corresponding shearing-resistance is *a₁b₁* on the autographic diagram. Hence, on the perpendicular at *o₁*, which is the projection of *c₁* on the horizontal axis, a length *o₁b₁'* equal to *a₁b₁* is marked off; then *o₁b₁'* will represent the shearing-resistance at *c₁* on the same scale as scale *A* of the autographic diagram.

Similarly, the shearing-resistance at *c₂*, which has a penetration of *d₂c₂* ($= Oa_2$), is *o₂b₂'* ($= a_2b_2$), that at *c₃* is *o₃b₃'* ($= a_3b_3$), that at *c₄* is *o₄b₄'* ($= a_4b_4$), and that at *c₅* is zero.

A smooth curve drawn through *b'*, *b₁'*, *b₂'*, *b₃'*, *b₄'*, and *o₅* will represent the distribution of shearing-resistance on the part of the cutting edge *Oc₅*, which is actually in action. Then if the area *Ob'o₅* under the curve is found by means of a planimeter and divided by 9 in., which is

the length of the projection of the cutting edge of the quadrant under consideration, the average shearing-resistance, \bar{p} , on the whole projection OR of the cutting edge is found.

Since the other three quadrants of the punch have identical conditions, \bar{p} will be the average shearing-resistance on the projection of the cutting edge of the whole punch, which is equal to πD in., where D is the diameter of the punch in in. It follows that the total shearing-

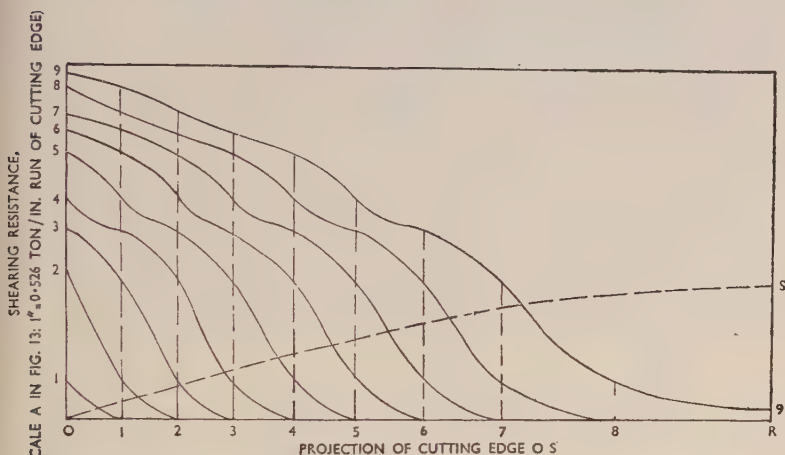


FIG. 14.—Graphical Solution of Shear Characteristics for 0.126-in. Mild Steel. (Clearance : nil. Punch diameter : 6 in. Shear : 0.032 in.)

resistance L corresponding to the overall penetration of the punch, OA , will be :

$$L = (\bar{p} \times f) \times \pi D \text{ tons}$$

where $f = 0.526$ ton per inch run of the cutting edge (scale A of the diagram in Fig. 13), since \bar{p} is in inches.

By taking fresh overall penetrations of the sheared punch and repeating the procedure described above, a series of curves similar to $b'b_1'b_2'b_3'b_4'o_5$ is obtained. These are shown as 1-1, 2-2, 3-3, 4-4, . . . &c., in Fig. 14 for the punch with 0.032 in. shear; while the derived curve is plotted in Fig. 15, which also contains the actual experimental curve with a punch of this shear. It will be seen that the two curves are very similar.

This graphical method has been applied to seventeen cases, covering different metals, clearances, and shears. In general, the predicted and measured values of maximum load and blanking work agree remarkably

well, and in very few cases did discrepancy in either respect exceed 10%. The best correlation was shown in the case plotted in Fig. 16.

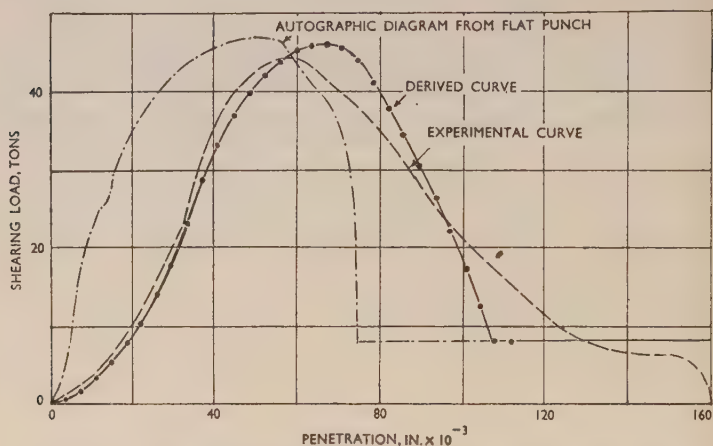


FIG. 15.—Experimental and Derived Curves for 0.126-in. Mild Steel.
(Clearance : nil. Punch diameter : 6 in. Shear : 0.032 in.)

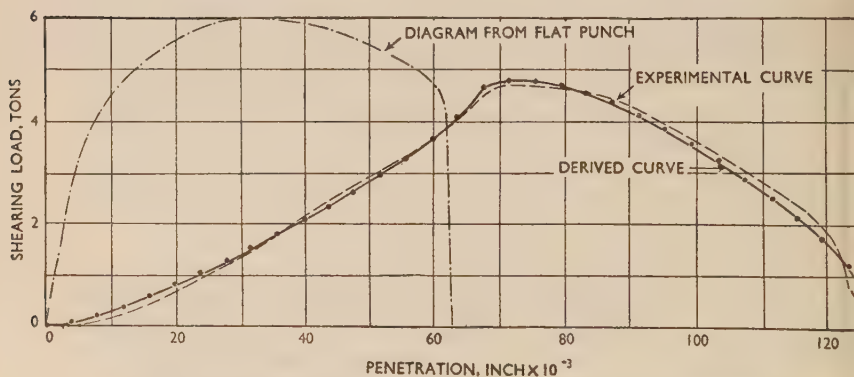


FIG. 16.—Experimental and Derived Curves for 0.080-in. Aluminium.
(Clearance : nil. Punch diameter : 6 in. Shear : 0.064 in.)

IV.—CONCLUSIONS.

(1) *Shear Fractures.*

The basic modes of fracture in blanking with circular tools are essentially the same as those found in the bar-shearing experiments. There is, however, an absence of incipient cracks on aluminium blanks, confirming that these would appear to be only edge effects on bars.

Multiple cracks form in shearing mild steel when the flow of metal is restricted either by blocking the ends of the bars or imposing hoop restrictions by confining the periphery of the blank in the blanking tool. Whenever multiple cracks occur, the shearing load is increased and greater work is required to blank the material through.

(2) *Effects of Clearance.*

With the exception of lead, the nominal ultimate shearing strength of all the metals tested decreases with increase of clearance. This decrease is most pronounced with clearances of less than 10%. With clearances greater than this, the fall in the shearing strength with the increase of clearance is approximately linear. For lead, the results are rather uncertain and the trend is obscure.

TABLE VI.—*Clearances Recommended for Least Work and Clean Fracture in Blanking.*

Material	Diamond Pyramid Hardness Number	Clearance Recommended, %
Cast Iron	213	5-10
Mild Steel	94-144	5-10
Brass (70 : 30)	77-110	0-10
Copper	64- 93	0-10
Zinc	61	0- 5
Aluminium	21- 28	0- 5
Lead	4.2- 6	0

The work done in blanking decreases first with increase in clearance and then remains steady or even rises. The fall is most rapid with clearances of less than 5%; while the work done in blanking aluminium and lead seems little affected by the change of clearance.

The clearances recommended for blanking with circular tools, in order to obtain a clean fracture with least strain work, are shown in Table VI. Since the metals in the table are arranged in order of decreasing hardness, it appears that a slightly greater clearance is preferable for harder materials.

(3) *Effects of Tool Curvature.*

There is a tendency for the shearing-resistance of materials, and the work to shear them through, to increase with increase in curvature of the tool.

The rate of fall in nominal ultimate shearing strength of materials with increase of clearance tends to become greater, if the diameter of the tool is reduced to very small values, e.g. $\frac{1}{4}$ in.

(4) *Effects of Shear.*

The fall in maximum blanking load with increase in shear is almost linear for most of the materials tested. As much as 75% reduction in the maximum load has been recorded in the tests.

Shear increases the punch penetration at maximum load and at failure, but smooths out the operation by eliminating shocks. The shearing work is also appreciably increased by the presence of shear for materials such as mild steel, cast iron, and brass, owing perhaps to the delay in the fall of load from the maximum as a result of the progressive nature of fracturing.

The characteristic curves for punches with any shear on them can be derived from the curve of a flat punch by a graphical method.

ACKNOWLEDGEMENTS.

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FRICTION IN WIRE DRAWING.*

1285

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SYNOPSIS.

The paper is divided into two main sections, the first containing the results of a short investigation of the magnitude of the frictional loss in drawing 65:35 brass wire, using carbide dies with and without parallel extensions. These results confirm the view that the process is the more efficient as the reduction of area becomes larger.

The second main section deals with the coefficient of friction between the wire and die calculated on the basis of the theories of Sachs, of Davis and Dokos, and of Hill and Tupper, respectively. The theories and results are compared, and it is shown that Davis and Dokos's theory can be used to obtain reasonably reliable values of the coefficient of friction under certain experimental conditions.

Experiments with "back-pull" have shown that the relationship between the die load and back-pull is not strictly linear, the small deviation from linearity being due to the fact that the coefficient of friction decreases as the back-pull is increased. In spite of this, however, it is believed that MacLellan's back-pull equation can be used to obtain accurate values of the coefficient under specified conditions.

The effects on friction of a number of variables have been investigated, using a variety of lubricants. Of these, the soaps provided relatively thick-film, or "quasi-hydrodynamic", lubrication, and even the liquid lubricants showed some hydrodynamic tendencies.

SYMBOLS USED IN THE PAPER.

A . . .	Cross-sectional area of wire.
L . . .	Length of wire.
Suffix $_1$. . .	Before deformation.
Suffix $_2$. . .	After deformation.
α . . .	Die semi-angle.
r . . .	Fractional reduction of area $\left(1 - \frac{A_2}{A_1}\right)$.
Suffix $_0$. . .	Drawing without back-pull.
ϵ . . .	True strain in tensile tests $\left(\log_e \frac{A_1}{A_2} = \log_e \frac{L_2}{L_1}\right)$.
<i>Stresses :</i>	
σ . . .	True stress in tensile tests.
W . . .	Drawing stress (= work done per unit volume).
W_F . . .	Drawing stress, without friction.
W_T . . .	Drawing stress, without friction and redundant work (assumed to equal the work done per unit volume in tensile stretching).

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Y_m	.	.	Mean yield stress (= mean ordinate of tensile true stress/true strain curve).
Y_1	.	.	Initial yield stress in Davis and Dokos's approximation to a tensile true stress/true strain curve $Y = Y_1 + K \log_e \frac{A_1}{A_2}$.

Coefficients :

K	.	.	Slope of linear approximation to true stress/true strain curve (see Y_1).
μ	.	.	Coefficient of friction.
b	.	.	Slope of back-pull/die load curve $\left(-\frac{dF}{dQ}\right)$.

Forces :

P	.	.	Drawing load.
F	.	.	Load on the die.
Q	.	.	Back-pull.

I.—INTRODUCTION.

THE object of the work described in this paper was the experimental investigation of various aspects of friction in the drawing of wire.

The experiments summarized in Section II were carried out in an attempt to obtain quantitative data regarding the amount of work wasted in overcoming frictional drag, both in the die and in the parallel extension.

In wire-drawing the drawing stress, in the appropriate units, is equal to the work done per unit volume of wire drawn (for instance tons/in.² = in.-tons/in.³). This stress can be considered to be made up of three components :

(a) The work done per unit volume in "homogeneous" deformation* of the wire in the die.

(b) "Redundant work" per unit volume, due to strains which do not contribute directly to the reduction of area.

(c) The work done per unit volume which is wasted in friction at the die/wire interface.

If the drawing stress, W_0 , is found experimentally, and factors (a) and (b) can also be determined, the frictional loss (c) can be obtained by difference :

$$(c) = W_0 - (a) - (b)$$

Component (a) is the ideal drawing stress, in which "redundant work" and friction are zero,* and it will be *assumed* that this is equal to the work done per unit volume in effecting the same reduction of area by simple tension. There is evidence^{1,2} that in homogeneous deformation the work done is the same whether the stress system is uniaxial, as in pure tension, or complex, as in drawing, where one

* An unattainable ideal.

principal stress is tensile, the others compressive. This assumption is also implicit in the more important mathematical theories of drawing.

Component (b), the redundant work, is more difficult to determine; there is, in fact, no method by which it can be measured with accuracy. Hill and Tupper³ have, however, shown theoretically that this factor decreases, and eventually becomes zero, when the die-angle is decreased and the reduction of area increased. This is in qualitative agreement with experimental results obtained by Linicus and Sachs,⁴ which show that there is little redundant work when the wire-drawing conditions are normal; and that it can be made negligibly small when the reduction of area is large and the die-angle small. In the present experiments, the errors in the estimated amounts of redundant work may be expected to have only a small effect on the results.

Attention was next devoted to the measurement of the coefficient of friction between the wire and the die and this is discussed in Section III. A mathematical analysis of some sort must be used to derive this coefficient from wire-drawing experiments, and this part of the paper is concerned almost as much with theories of wire drawing as with friction itself. The literature contains a large number of mathematical papers; it is increasingly clear, in fact, that in recent years theory and speculation have outstripped experiment. A number of calculations of the coefficient of friction, μ , are to be found in the theoretical papers; estimates which, in many cases, are based on somewhat doubtful experimental data, the results varying from $\mu = 0.001$ to $\mu = 0.6$. There is no agreement then even on the order of magnitude, and practically nothing is *known* of the effect of experimental variables on its value.

The different theories of wire drawing provide equations in which the drawing stress is expressed as a function of a number of variables, of which μ is the only unknown, and can therefore be calculated if the drawing stress is determined. To obtain accurate results much preliminary work is, however, needed, not only to measure the die-angles, to investigate the stress/strain properties of the wire, &c., but also to decide between the various theories propounded.

A second method of deriving μ is from back-pull experiments, the chief advantage of which is that it demands no knowledge of the properties of the wire. The formulæ which may be used are again based on wire-drawing theory, but are relatively simple and contain few terms. The advantages of the back-pull method are thus obvious, but there are a number of attendant disadvantages which are less apparent.

Linicus and Sachs⁴ have also calculated μ from experiments with rotating dies, and obtained a simple equation by which μ can be derived. The values so obtained were reasonable and consistent, but subsequent

work by Francis, Greenwood, and Thompson⁵ has shown that the method is of very doubtful reliability. At low speeds of drawing, the reduction in the drawing load when the die is rotated is so great that it cannot possibly be due simply to a decrease in friction; whilst at high drawing speeds rotation of the die may actually cause an increase in the load, which would be quite impossible according to Linicus and Sachs.

Still another method of calculating μ has recently been developed by MacLellan.⁶ The die is split longitudinally into two halves, and the drawing load measured together with the force tending to split the die. A simple analysis shows that μ can be calculated if these forces and the die-angle are known. This is a very promising approach, though there are still a few inherent difficulties; and no results have as yet been published.

II.—MAGNITUDE OF FRICTIONAL LOSS IN WIRE DRAWING.

1. *Apparatus.*

Two small experimental draw-benches were employed. In one, a $\frac{1}{4}$ -H.P. motor drove a revolving block, giving a constant drawing speed of 3.5 ft./min.; the second, which utilized the straining mechanism of an old tensile-testing machine, gave variable speeds from 0.004 to 3.3 in./min.

The device used to measure the load on the die (which equals the drawing load when there is no back-pull) is shown in Fig. 1 (Plate XLIX). The load on the die deflects one arm of a U-spring, and the deflection, indicated by a dial gauge, is a measure of the force. The instrument was calibrated by dead loading, the relationship between force and deflection being linear; a load of 0.51 lb. gave a deflection of 1 division (0.001 in.). The maximum load that could be measured on this scale was 115 lb., and for higher loads the die was placed lower down the arm of the spring to give a smaller bending moment.

Back-pull, where used, was applied by dead weights suspended on a Bowden cable clamped to the wire. The cable itself passed over a pulley mounted on ball bearings, and no friction could be detected even with the maximum load applied. Carbide dies were used throughout, all of which were made by the same firm and were in new condition, the finish of the bearing surfaces appearing to be uniformly excellent.

After some preliminary work, a satisfactory technique was evolved for obtaining the profiles of the dies from impressions made with a standard thermoplastic dental material known as "Compo". The die was first coated with a very thin film of Vaseline to prevent adhesion, and then preheated in warm water to about 45° C., the "Compo"

being heated in water until it became sufficiently plastic (about 55°C.). The impression was then taken, and the die allowed to cool, the impression being withdrawn before the die had become quite cold. When cold, the end face of the throat of the impression was lightly filed until it coincided with the narrowest part of the throat, an operation requiring careful examination under a low-power microscope. The die and

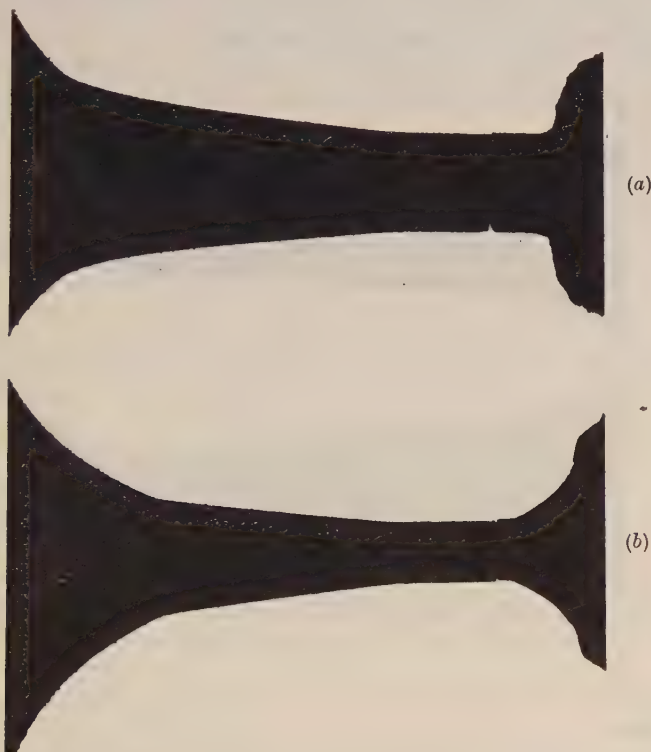


FIG. 2.—Typical Profiles of Dies with Parallel Extensions. $\times 8$.

(a) Die 4325W; 0.064 in. dia. (b) Die 4323W; 0.039 in. dia.

impression were then dried, the impression again fitted into the die, and warm dry "Compo" forced into the re-entrant cone of the die to complete the profile. The two parts of the impression could then be fitted together and photographed, with the necessary precautions to avoid distortion, some typical results being shown in Figs. 2 and 3.

Wistreich has recently proposed "Zeelex" for making such die impressions.⁷ This material is, however, mechanically weak, and since the dies used in the present experiments had long and slender profiles,

the "Zeelex" impressions could not be withdrawn without distortion or fracture.

The measurements particularly required are the lengths of the parallel extensions and the die-angles. In practice, however, the die throat is invariably "radiused", and the "cone" itself often slightly curved. The "effective" die-angles decrease, therefore, as the reduction of area of the wire decreases, and ultimately tend to zero, an important point which has often been overlooked.

The inaccuracy of measurement of the effective die-angles is probably as high as $\pm 8\%$, and in comparison with this any errors due to the



FIG. 3.—Typical Profiles of Dies without Parallel Extensions. $\times 8$.

(a) Die 5127W; 0.047 in. dia. (b) Die 5125W; 0.047 in. dia.

slight contraction of the "Compo" impression during cooling are quite negligible.

Good-quality soaps have given the most reproducible results, and for this reason have been mainly employed as lubricants. Three different soaps, *A*, *B*, and *C*, were used. Soap *A* is described as a "sodium soap of tallow and nut oil"; *B* is the "soap No. 3535" frequently referred to in papers by Thompson and Francis, and *C* is "Crosfields Brown" wire-drawing soap. It was found that there was little to choose between soaps *B* and *C*, and that *A* was inferior to both.

A number of liquid lubricants have also been employed, castor oil (medicinal quality), R.O.D. emulsion, "Oil-Dag" (concentrated), and "Hypoid 90". The R.O.D. emulsion is an aqueous wire-drawing lubricant, which finds application in the drawing of copper-base wires.

It is supplied as a paste, and was diluted to form a 10% solution. "Oil-Dag" is the well-known graphitoidal suspension in oil, and "Hypoid 90" is an "extreme-pressure" oil lubricant intended for use in mechanical transmissions.

The soaps were applied by rubbing the wire thoroughly between two blocks, the liquid lubricants being applied to the wire with a cotton-wool swab.

Friction is the least controllable factor in wire drawing and, even when the utmost care is taken, some fluctuation of the drawing load always occurs. With good soap lubricants the readings were, however, reproducible to within ± 1 or 2%.

In order to limit the number of experimental variables, it was decided to use 65 : 35 brass wire in all the experiments. The wire, of 0.0644 in. dia., was all taken from the same coil of annealed material, the surface finish of which, a matter of prime importance in such experimental work, was very good.

2. Mechanical Properties of the Brass Wire.

To obtain quantitative data from the wire-drawing experiments to be described, it was first necessary to determine the complete tensile true stress/true strain curve of the annealed material.

Fig. 4 shows such true stress/true strain curves as far as the beginning of necking, both for the annealed wire and after drawing. In this figure they have been superimposed to form a composite graph, in which the curves for the drawn wires have as their origins the points on the strain ordinate which correspond to their respective diameters.

The annealed wire begins to neck at a strain of 0.37, and the problem of finding the curve beyond this point presents some difficulty. Even with full-sized test-pieces this problem has never been completely solved, and with smaller-diameter wires many of the methods suggested are out of the question.

The broken line in Fig. 4 is the envelope of the individual curves for the drawn wires, and it will be assumed that this envelope represents the continuation of the true stress/strain curve of the annealed wire. Now below the point of necking, the curve for an initially stretched wire merges smoothly into that for the original wire; therefore this assumption will be justified if two conditions hold. Firstly, the effect of wire drawing on the properties of the wire must be the same as that of tensile stretching. Secondly, the drawn-wire curves must merge smoothly into the continued curve of the annealed wire, i.e. the slope of the drawn-wire curve must become equal to the slope of the continued curve. These conditions will now be considered separately.

Linicus and Sachs⁴ have given a series of stress/strain curves for drawn wires, which suggest that wire drawing produces an effect on the tensile properties similar to that due to simple stretching when the reduction of area is large (greater than 30%), and the die-angles are small (less than 8°), as was the case in these tests. In other words, the two are equivalent when there are no redundant strains.

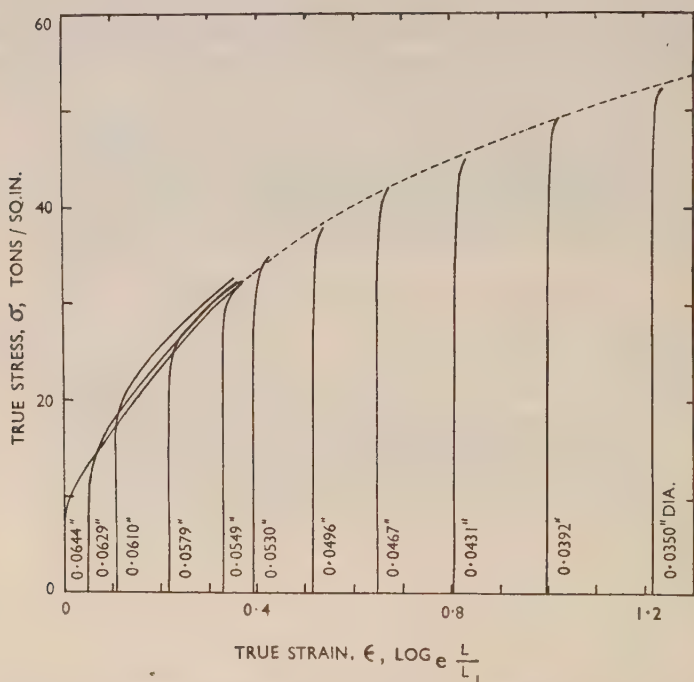


FIG. 4.—True Stress/True Strain Curves for 63 : 35 Brass Wire Drawn to the Diameters Shown.

The second condition cannot be correct, because it is impossible for the slope of the drawn-wire curve to become equal to the slope of the continued stress/strain curve. When a test-piece is being uniformly stretched, the slope of its true stress/true strain curve ($\frac{d\sigma}{d\varepsilon}$) is greater than the stress (σ), but as deformation proceeds, the slope decreases and the stress rises, and when the two become equal, necking must begin. Voce⁸ has recently proved this from geometrical considerations, and an alternative proof can be derived by approaching the problem from a

strain-hardening point of view. This phenomenon is illustrated in Fig. 5, which shows the experimental σ/ϵ and $\frac{d\sigma}{d\epsilon}\epsilon$ curves. Necking should take place when $\frac{d\sigma}{d\epsilon} = \sigma$, at 34 tons/in.². (That it actually occurs at 32 tons/in.² is probably due to the fact that the $\frac{d\sigma}{d\epsilon}$ curve is very sensitive to experimental errors.) In testing a wire drawn beyond this point, the slope of its true stress/strain curve can never equal the slope of the continued curve, because the drawn wire will neck when $\frac{d\sigma}{d\epsilon} = \sigma$, whereas in the continued curve $\frac{d\sigma}{d\epsilon} < \sigma$ (Fig. 5). Therefore the drawn wire will neck at a point below the continued curve, and the two cannot merge. The stress/strain curves, however, of the drawn wires reach a high stress with little deformation, and then bend round rapidly, whence the error should be small.

If the errors resulting from these two assumptions were additive the total might be serious, but fortunately they tend to offset one another, and the stress/strain curves of Linicus and Sachs suggest that the total inaccuracy is not large.

The rate of straining in the tensile tests was much slower than in most of the wire-drawing experiments, and serious errors would be involved in applying the results of Fig. 4 to the wire-drawing process if the rate of straining had a marked effect on the stress/strain characteristics of the material.

Manjoine and Náday⁹ in 1940 reviewed the literature on the effect of strain rate in tensile tests, and Gurney¹⁰ has referred to the more recent work. Agreement between the various published results is not very good, perhaps owing to the experimental difficulties involved in high-speed tests, but it is apparent that brass is one of the metals least affected by this variable, whereas copper, and some steels, are more susceptible. Even in the case of copper, however, the rate of strain, when varied over a wide range, has a relatively small effect on the room-temperature tensile properties.^{11, 12} This suggests that this variable can be neglected in the present experiments. Indirect evidence

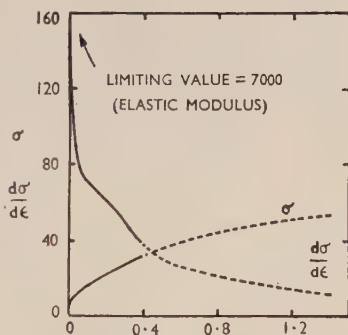


FIG. 5.—Complete σ/ϵ Curve and the Corresponding $\frac{d\sigma}{d\epsilon}/\epsilon$ Curve.
 σ = true stress. ϵ = true strain.

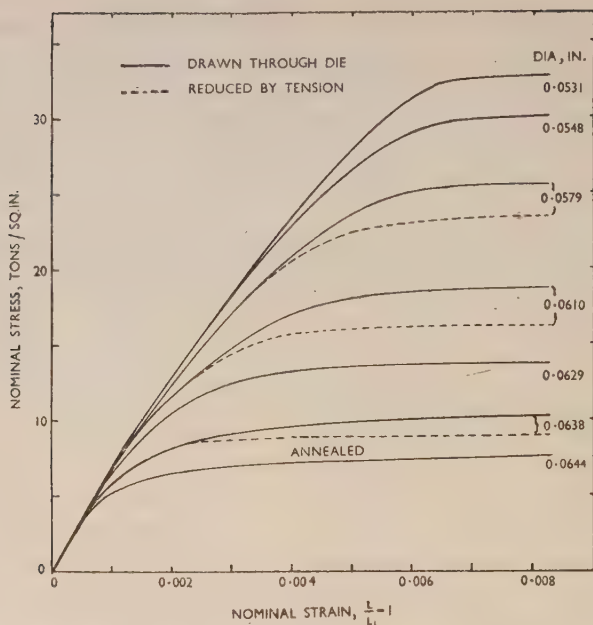


FIG. 6.—Stress/Strain Curves near the Elastic Region for Wire Drawn to the Diameters Shown.

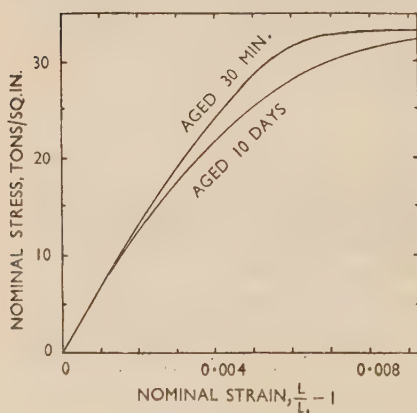


FIG. 7.—Showing Effect of Ageing after Drawing to 0.0531 in. Dia.

from creep tests on the brass wire, and also from back-pull tests to be discussed later, tends to confirm this view.

The strain axis of the complete stress/strain curve (Fig. 4) is on such a small scale that the apparent elastic limit is very misleading. Additional curves were, therefore, obtained for strains near the "elastic" range (Fig. 6). Tests were carried out on the annealed wire in the as-received condition and after drawing. (The diameters of

the wires before test are shown on the curves.) For comparison, broken curves are also shown for wires which had been initially stretched in ten-

sion to the same diameter as the drawn wires. In this graph the axes are nominal stress and nominal strain, but the strains are so small that these may be regarded as true stress and true strain without serious error.

It is evident from the differences between the wires initially drawn and stretched, respectively, that wire drawing has produced a greater equivalent strain than has the tensile stretching. In these tests the reduction of area in drawing was small, and some degree of redundant strain would, therefore, occur.

An unexpected ageing effect was noticed during this stage of the work, and is recorded as a matter of interest. The interval between drawing and testing affected some of the stress/strain curves near the elastic limit as is shown in Fig. 7. The conditions of drawing had a marked influence on this effect, but the phenomenon was not further investigated.

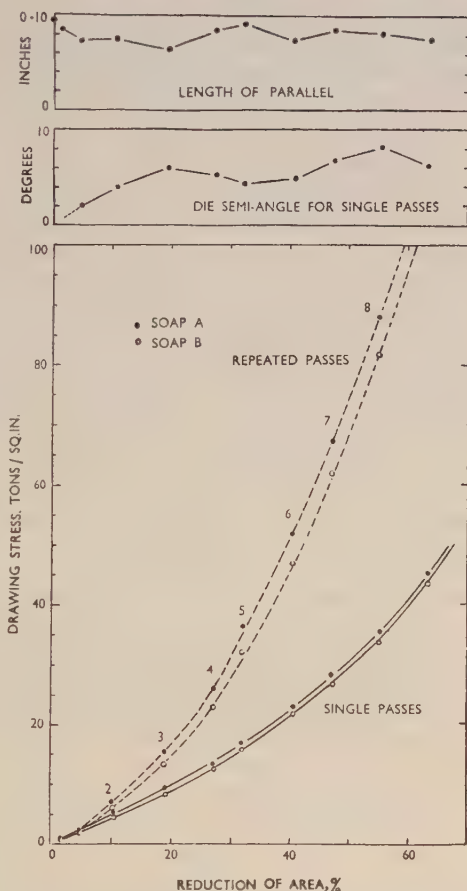


FIG. 8.—Total Drawing Stress/Reduction of Area Curves for Single and Repeated Passes for Brass Wire.

3. Work Wasted in Redundant Strain and Friction.

A number of experiments were carried out in which the work done in a single pass was compared with the total done in effecting the same reduction in repeated passes. Some of the results are given in Fig. 8, in which the drawing stress is plotted against the reduction of area, using dies with parallel extensions and a drawing speed of 3.5 ft./min.

The curves shown for repeated passes represent the sum of the individual drawing stresses, i.e. the total work done per unit volume. The wire was drawn down in steps, each step involving a separate experiment, and the process should not be confused with "cascade drawing", in which the wire is drawn through several dies simultaneously. The curves for single passes terminate at the point at which the wire breaks in drawing, i.e. when the ultimate tensile strength of the wire equals the drawing stress.

The effective die-angles and the lengths of the parallel extensions to the dies are shown at the top of the graph, and the importance of these will be realized when it is mentioned that all these dies were supposed to have the same die-angles and lengths of parallel.

In an essentially non-ageing material, the difference between the work done in single and repeated passes is due to two main causes, friction and redundant strain. The total frictional loss is greater with repeated passes owing to the parallel extensions, smaller effective die-angles, and greater interfacial pressures; whilst the redundant strain is increased because the reductions of area are smaller.

To obtain more quantitative information about the various components which make up the drawing stress, further experiments were carried out along the lines indicated in the introduction. The results obtained are shown in Fig. 9, in which the reduction of area abscissa has been abandoned in favour of the logarithmic strain scale, $\log_e \frac{A_1}{A_2}$.

To investigate the effect of the parallel extension, four similar dies, but without extensions, were obtained, with nominal dia. of 0.060, 0.055, 0.051, and 0.047 in., and with die-angles approximately the same as the corresponding ones with parallel extensions. The results given by these dies are indicated by the four points, marked with full triangles, on the curve for drawing stress "without parallel".

To supplement these four points, a method was devised to estimate the effect of parallel using dies which have parallel zones. In this method the wire was first drawn through the die and the drawing load measured. The drawn wire was then reintroduced into the same die, without further lubrication, and back-pull was applied to bring the drawing load up to the previous value. The difference between the drawing load and the back-pull, i.e. the load on the die, was then a direct measure of the additional force due to the parallel zone.

This procedure is valid only if the "parallel" zone is in fact perfectly parallel. The points estimated in this way (Fig. 9) agree fairly well with the other, direct determinations, but tend to underestimate the effect of the extension. This is presumably due to a slight taper in the

front of the extension, the taper being in the same direction as the die cone.

The curve in Fig. 9 showing the drawing stress "without redundant work and friction", W_T , was constructed from the true stress/true strain graph in Fig. 4. It has been pointed out that W_T can be taken

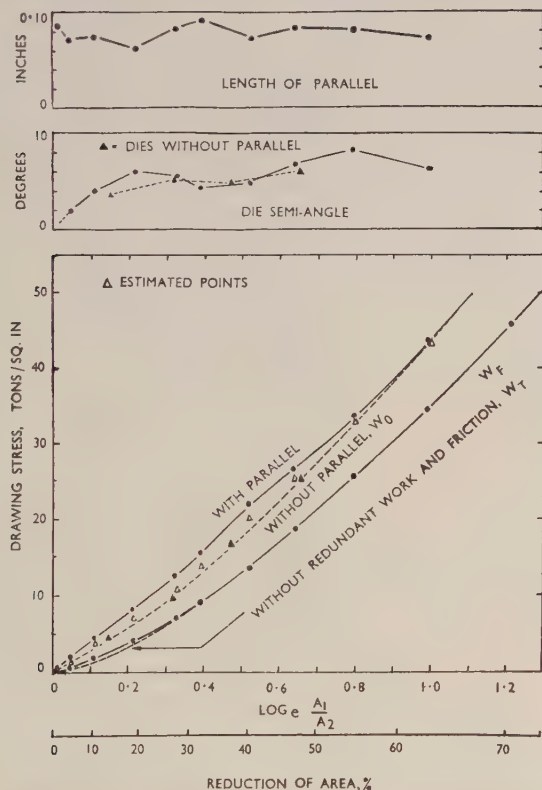


FIG. 9.—Effect of Parallel Extensions, Friction, and Redundant Work, on Drawing Stress. Lubricant: Soap B.

to be the work done per unit volume in tensile stretching, which, in turn, is equal to the area under the true stress/true strain curve.

The amount of redundant work for any given experimental conditions can be estimated from Hill and Tupper's theoretical analysis, but in preference to placing complete reliance on this theory, a simple experimental method suggested from a consideration of the work of Hill and Tupper³ and of Linicus and Sachs⁴ has been used.

Referring to the superimposed stress/strain curves in Fig. 4, it will be noticed that those for the drawn wires with dia. less than 0.053 in. do not fit perfectly into the curve for the annealed wire. On the other hand, if the wires are initially stretched in tension, the juxtaposition is perfect. To make the curves for the drawn wire coincide with the master curve for the annealed material, they must be moved along the ordinate to a higher strain value. This suggests again that drawing has strained the wire more than has tensile stretching, or, in other words, that in the drawing there has been redundant strain.

The wire drawn to 0.0610 in. dia. may be taken as an example (Fig. 10). The dia. 0.0610 in. corresponds to a natural strain of 0.104

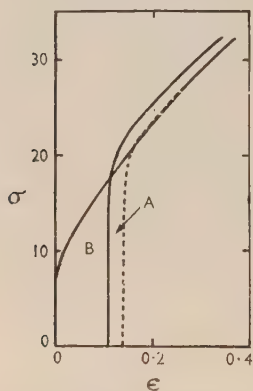


FIG. 10.—Illustrating Method used to Estimate Redundant Work.

A. Redundant work.

B. Work done in simple tension.

if the deformation is homogeneous, but to make the curves coincide, that for the drawn wire must be moved along to a strain of 0.14, as is shown by the broken line in Fig. 10. The difference between 0.104 and 0.14 may then be taken as a measure of the redundant strain, and the difference between the areas under the curves as representing the redundant work per unit volume.

This plausible procedure is based on two assumptions: firstly, that redundant strain in drawn wire causes an increase in strain-hardening equal to that due to the same strain in simple tension; and, secondly, that the work done per unit volume in effecting this increased strain is the same in each case. These assumptions appear to be reasonable, and may not be far from the truth, but that is the most that can be said for

them. Exactly the same assumptions are, however, implied in Hill and Tupper's method of calculating redundant work, in addition to basic theoretical assumptions which this experimental method avoids. The experimental approach gives rather higher values of the amount of redundant work than does the theoretical.

In Fig. 9 the amount of redundant work is represented by the difference between the curves for drawing stress "without friction" and "without redundant work and friction". It will be seen that the amount of redundant work is never very great, and becomes zero when the reduction of area reaches about 35%. It can be large only when the die-angles are large and the reduction of area small, and in these experiments all the die-angles were quite small, and,

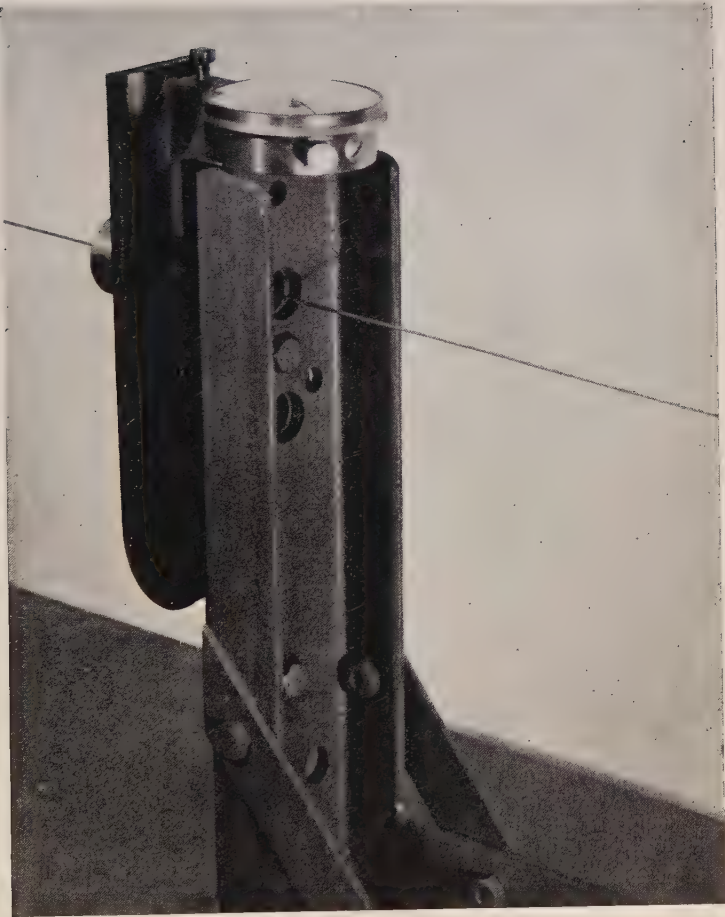


FIG. 1.—Photograph of Instrument Used to Measure the Drawing Load.



FIG. 27.—Showing Thickness of Soap Film on
Brass Wire Drawn from 0.0644 to 0.610 in.
Dia. $\times 10$.
Drawing speed : (a) 1000 ft./min., (b) 3.5 ft./min.

in addition, the effective die-angles decreased as the reduction of area fell.

The work per unit volume which is wasted in friction in the die cone and in the parallel extension is represented by the distance between the appropriate curves. Two important conclusions can be drawn from this graph. Firstly, the work wasted in friction in the die cone, when expressed as a fraction of the total drawing stress $\left(\frac{W_0 - W_F}{W_0}\right)$, decreases with increasing reduction of area. Secondly, the additional work due to friction in the parallel extensions, when similarly expressed as a fraction of the total, decreases with increasing reduction of area, and eventually becomes zero when the drawing stress approaches the ultimate tensile strength of the wire.

It is not proposed to attempt to explain these results in detail; any such attempt would be very involved and, it is felt, not very profitable, and it must suffice to indicate the broad lines on which an explanation may be sought.

The effective die-angles decrease as the reduction of area is decreased below 20%, causing a relative increase in the frictional drag in the die cone when the reduction of area is small. It will, however, be shown later that, with soap lubricants, the coefficient of friction decreases when the die-angle is decreased, and this will, to some extent, offset the effect of the die-angle on the frictional loss. If the die-angle and coefficient of friction are assumed constant, the results must be interpreted in terms of interfacial pressure, which varies in different parts of the die, its value at any point depending upon the axial tension and the yield strength of the wire. The results can, therefore, be interpreted only by using a mathematical analysis of the deformation, and the increase in yield strength caused by strain-hardening *must* be taken into account.

In the case of the frictional drag in the parallel zones, interpretation of the observed results is simpler. If the coefficients of friction and the lengths of the parallel zones are assumed to be constant, the frictional force is entirely dependent on the interfacial pressure. According to the maximum-shear-stress criterion of plastic flow, the interfacial pressure is equal to the difference between the axial tension and the yield stress of the wire, and, to a first approximation, the former may be assumed to be constant in all parts of the extension and equal to the drawing stress. The yield stress at any value of $\log_e \frac{A_1}{A_2}$ may be defined

as the ordinate of the tensile true stress/strain curve, if redundant strains are neglected. Therefore, if the complete true stress/strain curve in

Fig. 4 is traced over the drawing stress/strain curve, as is done in Fig. 11, the difference between the curves should be, and is, roughly proportional to the work wasted in the parallel extensions.

Referring again to Fig. 9, it will be seen that the slope of the ideal drawing-stress curve, W_T , increases with increasing reduction of area. In other words, the work done in tensile stretching per unit volume per unit increment of strain increases as the total strain increases. This affects the slope of all the other curves, and is, of course, due to strain-hardening.

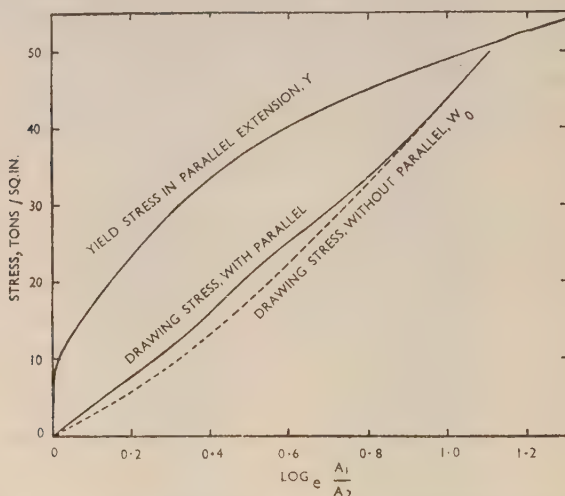


FIG. 11.—Plot of True Stress/Strain Curve over Drawing Stress/Strain Curve, Showing Work Wasted in Parallel Extensions.

III.—THE COEFFICIENT OF FRICTION IN WIRE DRAWING.

1. *Theories of Wire Drawing and their Application to the Calculation of the Coefficient of Friction.*

Wire-drawing theory provides one of the few methods available for the calculation of the coefficient of friction μ between the wire and the die. A large number of theories can be used, but fortunately MacLellan ⁶ has reviewed most of them, and those which are, for one reason or another, unsatisfactory can at once be eliminated. Of the remainder, the most important are that of Sachs, and Davis and Dokos's modification of it, and the recent theory of Hill and Tupper.

In the ensuing sections these theories will be outlined briefly, then

used to calculate μ from a number of experimental results, and finally discussed in an attempt to determine which seems to be the most reliable.

(a) *Sachs's Theory.*

In this, the oldest theoretical treatment, the drawing stress for dies without parallel extensions is given by the equation :

$$W_0 = \frac{P_0}{A_2} = Y_m \left(1 + \frac{1}{\mu \cot \alpha} \right) \left(1 - \left(\frac{A_2}{A_1} \right)^{\mu \cot \alpha} \right). \quad (1)$$

It is based, however, on the following assumptions :

(1) That the axial tensile stress is distributed evenly over the cross-section of the wire, and that the effect of interfacial friction is to increase this stress.

(2) That the axial, radial, and tangential directions are those of the principal stresses.

(3) That the maximum shear-stress criterion governs the plastic yielding of the wire. (But Lunt and MacLellan¹³ have shown that, under the assumed stress conditions, the more accurate maximum shear-strain-energy criterion gives the same result.)

(4) That the yield stress of the wire is constant, and equals the mean value, Y_m .

(5) Elastic strains are neglected.

Hill¹⁴ has pointed out that these assumptions imply that the wire is deformed homogeneously, and that the work of deformation is equal to that in uniform tension.

In order to calculate μ , the terms W_0 , α , A_1 , A_2 , and Y_m must be found, and, apart from Y_m , this presents little difficulty. The term Y_m originates in the maximum-shear-stress criterion, and is equal to the mean ordinate of the tensile true stress/true strain curve of the wire over the appropriate range of strain. This is equal to the area under the curve divided by $\log_e \frac{A_1}{A_2}$, or :

$$Y_m = \frac{\int_{A_2}^{A_1} \sigma d(\log_e A)}{\int_{A_2}^{A_1} d(\log_e A)} = \frac{W_T}{\log_e \frac{A_1}{A_2}} \quad . \quad . \quad . \quad (2)$$

This is the only logical method of finding Y_m , but although somewhat obvious does not seem to have been used before. In the past Y_m has sometimes been taken to be the average of the initial and final yield stresses of the wire, and has even been assumed to equal the ultimate tensile strength of the wire before drawing. This value of Y_m is of

great importance in calculating μ , since if, for instance, Y_m is altered by 15%, the calculated values of μ may be altered by as much as 300%.

It has been shown¹⁵ that when μ is zero in equation (1), the drawing stress becomes :

$$W_0 = \frac{P_0}{A_2} = Y_m \log_e \frac{A_1}{A_2} \quad . \quad . \quad . \quad . \quad (3)$$

and as μ tends to zero the drawing stress approaches this limit. If this equation is compared with equation (2) it will be seen that when friction is absent, the drawing stress W_0 (work done per unit volume in drawing)

is equal to W_T , the work done per unit volume in tensile stretching, a result to be expected from the assumptions made in Sachs's theory, and serving to confirm the correctness of the method of finding Y_m .

Lunt and MacLellan¹³ have recently modified Sachs's theory by introducing an improved co-ordinate system, the main effect of which is to make the proof more rigorous, but the final result is the same as equation (1).¹⁶

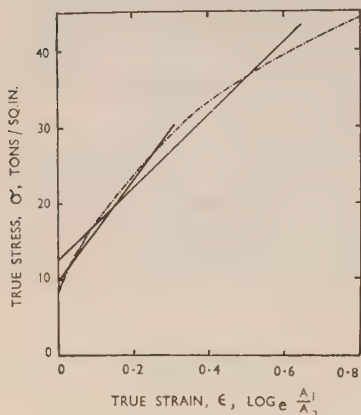


FIG. 12.—Showing Straight-Line Approximations to True Stress/Strain Curve for Brass Wire. (Davis and Dokos's method.)

(b) Davis and Dokos's Theory.

Davis and Dokos¹⁵ have also modified Sachs's theory to take strain-hardening into account, by

making the yield stress a function of the instantaneous area A . This refinement leads to the rather cumbersome equation :

$$W_0 = \frac{P_0}{A_2} = \left(1 + \frac{1}{\mu \cot \alpha}\right) \left\{ \left[1 - \left(\frac{A_2}{A_1}\right)^{\mu \cot \alpha}\right] \left(Y_1 - \frac{K}{\mu \cot \alpha}\right) + K \log_e \frac{A_1}{A_2} \right\} \quad . \quad (4)$$

In deriving this expression, it is assumed that Y is a linear function of the natural strain, i.e. :

$$Y = Y_1 + K \log_e \frac{A_1}{A} \quad . \quad . \quad . \quad . \quad (5)$$

To obtain the closest fit, the constants Y_1 and K must be altered as the reduction of area is altered. Fig. 12 shows two straight lines

for different reductions of area fitted to the true stress/strain curve for the annealed brass wire.

It is not difficult to show that the mean value of Y in (5) over the range from A_1 to A_2 is :

$$Y_m = Y_1 + \frac{K}{2} \log_e \frac{A_1}{A_2} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and in applying Davis and Dokos's equation in any particular case, Y_1 and K have been chosen both to fit the true stress/strain curve and also to make Y_m in (6) equal to Y_m in (2), used in Sachs's equation. This renders the results obtained from Sachs's equation strictly comparable with those from Davis and Dokos's equation, since the theoretical work of deformation is then the same in each case.

Davis and Dokos derived an expression from their theory for $\mu = 0$, which, when rearranged, becomes :

$$W_0 = \log_e \frac{A_1}{A_2} \left(Y_1 + \frac{K}{2} \log_e \frac{A_1}{A_2} \right) \quad . \quad . \quad . \quad . \quad (7)$$

and it is clear from equation (6) that this is the same as Sachs's equation (3) for $\mu = 0$. This is to be expected, since the assumptions made in the two theories are the same, except that the yield stress in Davis and Dokos's theory is not assumed to be constant.

It should be mentioned that Davis and Dokos do not use the maximum-shear-stress criterion of plastic flow, but their rather involved procedure amounts to much the same thing, and it can be shown that the same result is obtained when the shear-stress criterion is adopted. In their original equation they also include an additional term to take into account the "stress at the boundary between the elastic and plastic ranges". This empirical term spoils an otherwise useful equation, and has been omitted, since, as MacLellan ⁶ points out, there appears to be no justification for it. Even if this term were to be included, it would not affect the present results, since, according to the empirical procedure used by Davis and Dokos, its value in the present experiments is zero.

(c) *Hill and Tupper's Theory.*

Hill and Tupper ³ have recently developed a theory of wire drawing which differs entirely in its method of approach from its predecessors, and have attempted to formulate the actual strain configuration in the wire during deformation. This for three-dimensional wire-drawing conditions they were unable to do, and their analysis is for a two-dimensional "plane-strain" model. The analysis is based on a somewhat recondite theory of plane plastic strain and the theory of the slip-line field. One of the principal assumptions made is that the material

is "plastic rigid" (an idealized material which is perfectly rigid up to a given stress, and then flows plastically with no strain-hardening).

The chief triumph of the theory is that it predicts the amount of redundant strain for different combinations of die-angles and reductions of area. In order, however, to provide a general solution which can be applied to ordinary wire-drawing experiments, three further assumptions are made:

(1) It is assumed that the results of the two-dimensional analysis can be quantitatively applied to three-dimensional problems by means of semi-empirical corrections. Some evidence is adduced to support this.

(2) The approximation is made that friction does not affect the pressure on the die wall.

(3) In taking into account the effect of work-hardening it is implied that the yield stress is constant in all parts of the die and equal to the true mean value.

The final solution is given by the simple formula:

$$W_0 = \frac{P_0}{A_2} = (1 + \mu \cot \alpha) W_F \quad . \quad . \quad . \quad (8)$$

where W_F is the drawing stress without friction. To find W_F the true stress/true strain curve of the wire is used in conjunction with Fig. 9 of Hill and Tupper's paper,³ which gives the "equivalent strain" for any given die-angle and reduction of area. The drawing stress without friction, W_F , is then the area under the true stress/strain curve of the wire up to this strain. Hill and Tupper justify this procedure by their concept of a generalized stress/strain curve for all types of loading.

In ordinary wire-drawing practice the conditions are such that there is usually little or no redundant strain (see pp. 416-417), and hence $W_F = W_T$. From equations (2) and (8) it will be seen that Hill and Tupper's equation then becomes:

$$W_0 = \frac{P_0}{A_2} = (1 + \mu \cot \alpha) Y_m \log_e \frac{A_1}{A_2} \quad . \quad . \quad . \quad (9)$$

If $\mu = 0$, the drawing stress becomes equal to the work done per unit volume in tensile stretching, as in Sachs's equation (3). An interesting feature of equation (9) is its close resemblance to Lewis's empirical wire-drawing formula, and the fact that Sachs and Van Horn¹⁷ have proposed the same equation as a simple working guide for practical use.

If there is no redundant strain, the difference between the theories of Hill and Tupper and of Sachs decreases as $\mu \cot \alpha$ decreases, Hill and Tupper's formula, however, always predicting the higher drawing stress, i.e. lower calculated values of μ . The basic reason for this difference is

that in Sachs's equation friction is assumed to decrease the pressure on the die wall, whereas in Hill and Tupper's equation this effect is neglected.

(d) *Results.*

A series of drawing experiments was carried out in which the drawing stress was determined for different values of the reduction of area and die-angle, and for different lubricants. The drawing speed was 3.5 ft./min., and the wire used was the 0.0644 in. dia. annealed brass. For each experiment μ was calculated from the equations of Sachs, of Davis and Dokos, and of Hill and Tupper.

TABLE I.—*Drawing Stress for Different Values of r and α , Using Soap B.*

Dies without parallel extensions. Drawing speed : 3.5 ft./min. Material : annealed brass wire 0.0644 in. dia.

Reduction of Area, r	Die-Angle, α	Drawing Stress, W_0	μ^*			Constants used in Equations †				
			Sachs	Davis and Dokos	Hill and Tupper	W_F	W_T	Y_m	Y_1	K
0.135	3.5°	4.3	0.040	2.60	2.27
0.27	5.5°	9.6	0.060	0.056	0.046	6.5	6.5	20.6	10.4	65
0.37	5.0°	16.5	0.062	0.054	0.040	11.3	11.3	24.4	11.2	57
0.48	6.1°	25.1	0.067	0.060	0.036	18.7	18.7	28.7	13.05	48
0.47	3.0°	25.6	0.044	0.033	0.021	18.2	18.2	28.3	12.9	48
0.465	4.4°	24.4	0.058	0.048	0.030	17.5	17.5	27.9	12.9	48
0.48	6.1°	25.1	0.067	0.060	0.036	18.7	18.7	28.7	13.05	48
0.435	11.0°	20.6	0.12	0.11	0.070	15.2	15.2	26.6	12.9	48

* The values of μ believed to be the most reliable are set in heavy type.

† A list of symbols is given at the beginning of the paper. W_0 , W_F , W_T , Y_m , and Y_1 are in tons/in.²

Table I shows the results obtained, with Soap B as the lubricant, for various reductions of area and die-angles. The different constants used in the equations are shown at the right-hand side of the table, these constants being obtained from the true stress/true strain curve of the wire by the methods already described. All the values of μ fall within the range 0.021–0.12, and most of them between 0.033 and 0.067. This range is much smaller than might be expected from a consideration of the wide differences between the respective theories, and between the experimental variables.

Similar tests were then carried out with different lubricants but using only three dies, with the results shown in Table II. In both these tables it has been assumed that there was no redundant strain, except in the one case, in Table I, where the reduction of area is only 13.5%.

Davis and Dokos's equation gives slightly lower values of μ than does that of Sachs, but on the whole the agreement is quite good. In

TABLE II.—*Drawing Stress for Different Values of r and α , Using Various Lubricants.*

Dies without parallel extensions. Drawing speed : 3.5 ft./min. Material: annealed brass wire 0.0644 in. dia.

Reduction of Area, r	Die-Angle, α	Lubricant	Drawing Stress, W_0	μ *			Constants used in Equations				
				Sachs	Davis and Dokos	Hill and Tupper	W_F	W_T	Y_m	Y_1	K
0.273	2.8°	Soap B	11.3	0.051	0.042	0.035	6.6	6.6	20.5	10	65
		R.O.D.	13.2	0.078	0.067	0.049					
		emulsion									
		Castor oil	13.7	0.087	0.072	0.053					
		Oil Dag	14.8	0.10	0.088	0.061					
0.47	3.0°	Hypoid 90	15.8	0.13	0.10	0.068					
		Soap B	25.6	0.044	0.033	0.021	18.2	18.2	28.3	12.9	48
		R.O.D.	30.3	(0.10)	0.064	0.035					
		emulsion									
		Castor oil	30.8	(0.11)	0.069	0.036					
		Oil Dag	33.4	?	0.095	0.044					
0.48	6.1°	Hypoid 90	34.2	?	0.105	0.046					
		Soap B	25.1	0.067	0.060	0.036	18.7	18.7	28.7	13.05	48
		R.O.D.	26.7	0.091	0.077	0.046					
		emulsion									
		Castor oil	27.1	0.098	0.081	0.048					
		Oil Dag	28.3	0.12	0.096	0.055					
		Hypoid 90	29.4	0.14	0.11	0.061					

* The values of μ believed to be the most reliable are set in heavy type.

some results in Table II, however, where the die-angle is small and the reduction of area large, Sachs's equation failed completely, and no matter how large μ was made, the equation would not give a drawing stress as high as that actually required. This was unexpected, and apparently has not been noticed before.

TABLE III.—*Effect of Surface Finish.*

Condition of Die	Lubricant	Drawing Stress, W_0 , tons/in. ²	μ (Davis and Dokos)
Worn-in	Soap B	26.1	0.036
	Castor oil	30.8	0.069
Rough-lapped	Soap B	26.8	0.040
	Castor oil	38	0.16

The dies used in these tests were without parallel extensions; they were in new condition but had been "worn-in". It was found with these dies and the soap lubricant that the drawing load gradually decreased as the die was used, and eventually reached a minimum. After this, the results were reproducible to within ± 1 or 2%. The phenomenon may be due to the removal of the minute furrows in the die cone caused by the polishing, or to the filling up of pores in the

sintered carbide, into which the lubricant would be forced under the high pressure. Some experiments on the effect of surface finish support the latter explanation. The drawing stress was first measured using a good, "worn-in" die, which was then lapped circumferentially with a coarse-grade, carborundum abrasive (240 mesh), and the experiment repeated. The die-angle was 3.0° and the reduction of area 45%; the results are shown in brief in Table III.

With castor oil the surface finish has a big influence on μ , as might be expected, but with the soap there is practically no change.

(e) *Discussion.*

The main object of this discussion is to determine the most reliable values of μ , and to this end it is necessary to examine the possible sources of error, and to decide which theory seems the most accurate.

The experimental methods used to find the terms in the equations have already been described, and all of these terms will include (small) experimental errors. The total effect, however, should not be serious, and the error in μ so arising should be less than 0.01.

A more important possible source of error is the assumption in all but one of the results in Tables I-III, that there is no redundant strain. According to Hill and Tupper's theoretical work this assumption is justified, but evidence from the series of stress/strain curves provided by Linicus and Sachs suggests that there is, in fact, an appreciable amount of redundant strain in the case of the 11° die-angle and the 13.5% and 27% reduction of area included in Table I. These results will, therefore, be neglected. Redundant strain cannot be measured with a known degree of accuracy, and all that can be done is to make sure that it is very small, and then assume that it is, in fact, zero.

The effect of small errors in the assumption that the work of deformation in drawing, W_F , equals the work done in tension, W_T , can best be illustrated by an example. If W_F is taken to be 18.7 in.-tons/in.³, $r = 0.48$, and $\alpha = 6.1^\circ$ (Table II), and two different lubricants give values of μ , according to Davis and Dokos's equation, of 0.10 and 0.015 respectively, then if the true value of W_F is 20.0 the values of μ become approximately 0.09 and 0.003. In each case the error is only about 0.01, but it should be noticed that the percentage error when μ is very small is quite large.

It is concluded that any small error due to the assumption that redundant work is zero will make the calculated values of μ slightly too large; and that it is not advisable to calculate μ by this method when μ is small, say less than 0.03.

When there is no redundant work, the deformation is homogeneous

and the work done per unit volume in causing this deformation can be taken to be the same as that in tensile stretching. This is in accord with the premises underlying both Sachs's and Hill and Tupper's equations. Which theory, then, should be used? Evidence from Table I of Hill and Tupper's paper³ suggests that Sachs's equation is more accurate than their own. This table provides a series of numerical results which have been derived from their theory of plane strain, and the theoretical drawing stress and the pressure on the die wall are given for different values of μ , α , and reduction of area. The results show clearly that an increase in μ causes the interfacial pressure to decrease with all die-angles, and this is especially marked when the angle is small. Yet in their general formula (equation (8)) they have assumed that friction does *not* affect the interfacial pressure, and justified this by claiming that the error is not serious.

Some calculations have been made in which Sachs's equation (1) was applied to the results in Hill and Tupper's table, and it was found that for die-angles of less than 10° the drawing stress by Sachs's formula (1) was much closer to their theoretical drawing stress than that calculated from their own general formula (8). With die-angles greater than 10° , Sachs's theory could not be used because of redundant strain. In applying this equation of Sachs, the semi-empirical corrections suggested by Hill and Tupper were used to convert the two-dimensional results to three-dimensional.

To illustrate this point an example may be given. For $\alpha = 10^\circ$, $\mu = 0.126$, and $\frac{A_1}{A_2} = 1.316$, Hill and Tupper give the theoretical ratio of drawing stress to yield stress $\left(\frac{W_0}{Y_m}\right)$ as 0.446. Using their general equation, $\frac{W_0}{Y_m} = 0.487$. Employing Sachs's equation, $\frac{W_0}{Y_m} = 0.431$, and if the very small amount of redundant strain which is present is taken into account, this figure becomes even closer to the theoretical value of 0.446.

Having concluded then that Sachs's equation is to be preferred *in these circumstances*, it must now be decided whether Davis and Dokos's modification is an improvement on the original Sachs theory. The only fundamental difference between the two is that Davis and Dokos have allowed for strain-hardening in a manner which is probably close to the truth, whereas in the original the yield stress is assumed constant in all parts of the die. The question will not be discussed at length because this seems to the present authors to be a sufficient *a priori* reason to prefer Davis and Dokos's theory.

The difference between the results obtained by these two theories is appreciable but not large. However, in the exceptional case, Sachs's equation fails completely. It will be noticed in Table II that when this occurs, the actual drawing stress, W_0 , exceeds the mean yield stress of the wire, Y_m . This is a fundamental absurdity when applied to Sachs's theory, since, if the yield stress is assumed to be constant, the wire must break when the drawing stress is higher than the yield stress. Davis and Dokos's equation is, of course, not open to the same objection, and can be applied to any real wire-drawing problem.

It is interesting to consider this matter further. In Sachs's equation it has been pointed out that when $\mu = 0$ the drawing stress :

$$W_0 = Y_m \log_e \frac{A_1}{A_2},$$

but when μ is infinitely large :

$$W_0 = Y_m.$$

If W_0 is plotted against μ for otherwise standard conditions, it is found that W_0 increases to a maximum and then decreases asymptotically towards the limiting value Y_m , as μ is made very large. The precise position of the maximum depends on the die-angle and reduction of area.

In Davis and Dokos's equation no such maximum is found, and it has been shown from equations (6) and (7) that when $\mu = 0$:

$$W_0 = Y_m \log_e \frac{A_1}{A_2}$$

as before. But as μ is increased, W_0 rises, rapidly at first, and then asymptotically towards the limiting value for $\mu = \infty$:

$$W_0 = Y_1 + K \log_e \frac{A_1}{A_2}$$

In their theory this expression is the yield stress of the drawn wire.

A graphical comparison of the theories is provided by Figs. 13–15, which show the theoretical W_0/μ relationships for three sets of experimental conditions from Tables I and II. It may be noted that only one of the curves shows the maximum associated with Sachs's equation (Fig. 14). In the other curves the maxima would occur at

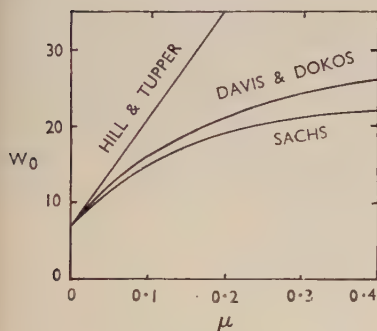


FIG. 13.—Effect of μ on Theoretical Drawing Stress W_0 .

Reduction of area $r = 0.273$.
Die angle $\alpha = 2.8^\circ$.

very high values of μ , and are off the graphs. The maxima are found at low values of μ when the reduction of area is large and the die-angles small, and in these circumstances Sachs's equation is almost useless. In other words, when the drawing stress approaches the mean yield stress, his equation becomes seriously inaccurate, and when the drawing stress is much greater than the yield stress, the equation fails completely.

It is concluded, then, that Davis and Dokos's equation should be used when there is little or no redundant strain. Values of μ calculated

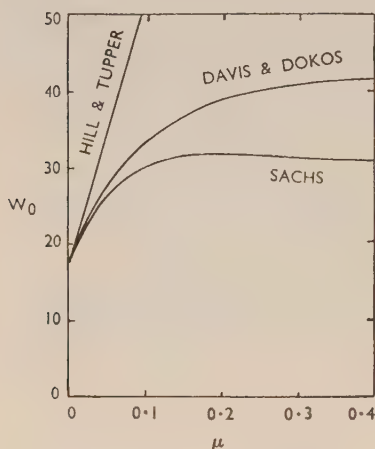


FIG. 14.—Effect of μ on Theoretical Drawing Stress W_0 .

Reduction of area $r = 0.47$.
Die angle $\alpha = 3.0^\circ$.

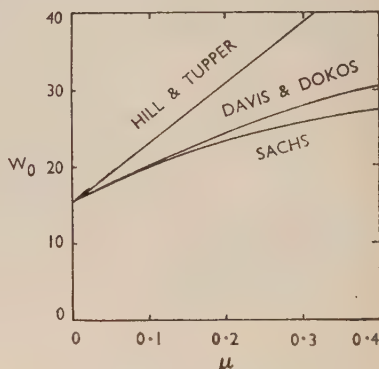


FIG. 15.—Effect of μ on Theoretical Drawing Stress W_0 .

Reduction of area $r = 0.435$.
Die angle $\alpha = 11.0^\circ$.

from this equation, and using what are believed to be the most reliable results, are set in heavy type in Tables I and II.

In the different theories it is implied that μ is constant in all parts of the die. When well-polished dies are used, this assumption is almost certainly close to the truth, and no serious error need be expected from this source.

Elastic strains are neglected in all these theories, and this possible source of error remains to be examined. It is difficult to see why this assumption should involve appreciable errors, because in normal wire drawing the plastic strain is many thousand times greater than the maximum possible elastic strain. The only available criterion by which the magnitude of the error involved can be estimated is on the basis of the theory of Davis and Dokos.

It has been pointed out that the additional elastic term in this

theory is empirical and unconvincing, and has so far been omitted. Davis and Dokos assumed that elastic strains create a back-pull effect, and that this back-pull is equal to the load at which the extrapolated drawing load/reduction of area curve intersects the ordinate. But in the present work this type of curve extrapolates essentially to the origin (see Fig. 8),* and hence there will be little or no back-pull, and the error (due to neglecting elastic strains) according to Davis and Dokos will be negligible. For the sake of argument, however, let us assume the improbable, and take it that elastic strains cause a back-pull which is equal to the limit of proportionality of the wire, 3 tons/in.² (Fig. 6); the calculated values of μ in Tables I and II will then become about 25% smaller.

To sum up, possible sources of error have been examined, and there seems good reason to believe that these errors are small, their effect being, however, to make the derived values of μ too large. The results in heavy type in Tables I and II are regarded as reliable, and though slightly too high, the error should not, in the opinion of the present authors, be more than 30% at most.

2. Back-Pull Experiments and Their Application in Calculating the Coefficient of Friction.

When wire is drawn without back-pull the load on the die equals the drawing load :

$$P_0 = F_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Thompson¹⁸ showed that when a backwards force is applied to the wire on the entrance side of the die, the load on the die falls, and from statical considerations the sum of the back-pull and the die load must equal the drawing load :

$$P = F + Q \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

It was further found experimentally that the relationship between F and Q was strictly linear, or that :

$$F = F_0 - bQ = P_0 - bQ \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The "back-pull factor", b , which is the slope of the F/Q curve, varies with the experimental conditions.

The theories of wire drawing can be extended to provide theoretical expressions for b . It is found that b is dependent only on μ , r , and α , and because these terms, apart possibly from μ , do not alter when the back-pull is varied, the theories confirm that the relationship between F and Q should be linear. The effect of this back-pull is to decrease the

* Cf. Francis and Thompson, *J. Inst. Metals*, 1931, **46**, Fig. 7, p. 321, where it is suggested that this intercept is, in the main at any rate, determined by the frictional loss.

interfacial pressure between the wire and the die, hence the frictional force and the load on the die decrease.

If, then, b is found by experiment, μ can be calculated, and the advantage of this method lies in the fact that it is not necessary to know anything about the stress/strain properties of the material.

(a) *Theories of Drawing with Back-Pull.*

MacLellan ⁶ has extended Sachs's theory to obtain an equation for the back-pull factor:

$$b = 1 - (1 - r)^{1 + \mu \cot \alpha} \quad . \quad . \quad . \quad (13)$$

It is not widely recognized that Davis and Dokos ¹⁵ derived exactly the same expression at an earlier date using their own theory of wire-drawing, though the result is given in a different form. The fact that the theories both of Sachs and of Davis and Dokos yield the same back-pull equation shows that this is independent of strain-hardening.

Hill and Tupper's theory of wire drawing has also been extended to provide an expression for b (Hill ¹⁴):

$$b = r(1 + \mu \cot \alpha) \quad . \quad . \quad . \quad (14)$$

This also is independent of strain-hardening, but in all other respects the assumptions are unchanged.

These equations are only concerned with the slope b of the F/Q curve; they say nothing about the actual value of the die load F .

Hill has pointed out that in both these equations b approaches the limiting value r as $\mu \cot \alpha$ tends to zero, and conversely, that the difference between the two equations increases as $\mu \cot \alpha$ (and r) are increased. According to equation (13), b must always lie between 0 and 1, whereas there is no upper limit to b in equation (14).

In deriving values of μ from die load/back-pull curves, equations (13) and (14) will be used, but in discussing the results it is necessary to know the complete equations for drawing with back-pull. Sachs's complete equation is obtained quite simply by combining (1), (12), and (13):

$$F = A_2 Y_m \left(1 + \frac{1}{\mu \cot \alpha}\right) \left[1 - \left(\frac{A_2}{A_1}\right)^{\mu \cot \alpha}\right] - Q \left[1 - \left(\frac{A_2}{A_1}\right)^{1 + \mu \cot \alpha}\right] \quad . \quad (15)$$

Similarly, Davis and Dokos's equation is obtained by combining (4), (12), and (13):

$$F = A_2 \left(1 + \frac{1}{\mu \cot \alpha}\right) \left\{ \left[1 - \left(\frac{A_2}{A_1}\right)^{\mu \cot \alpha}\right] \left(Y_1 - \frac{K}{\mu \cot \alpha}\right) + K \log_e \frac{A_1}{A_2} \right\} - Q \left[1 - \left(\frac{A_2}{A_1}\right)^{1 + \mu \cot \alpha}\right] \quad . \quad (16)$$

and Hill and Tupper's equation, by combining (8), (12), and (14), becomes :

$$F = W_F A_2 (1 + \mu \cot \alpha) - Qr(1 + \mu \cot \alpha) \quad . \quad . \quad (17)$$

(b) *Effects of the Die-Angle and the Reduction of Area.*

A series of experiments was planned to investigate the effects of the die-angle and the reduction of area on the die load/back-pull relationship, and so on the calculated values of μ . Dies without parallel extensions were used, and the drawing speed was again 3.5 ft./min.

In these and subsequent experiments, the annealed brass wire was

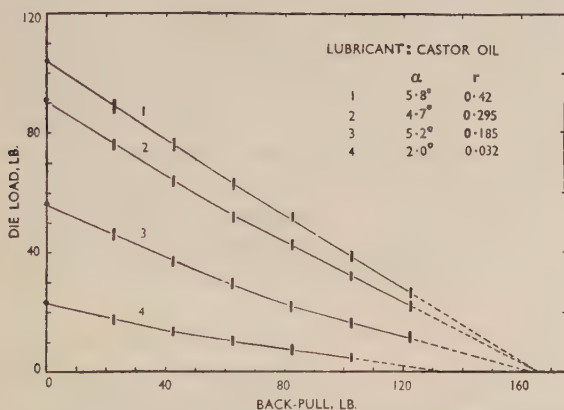


FIG. 16.—Influence of Reduction of Area on Die Load/Back-Pull Curves.
Drawing speed : 3.5 ft./min.

initially drawn from 0.0644 to 0.0610 in. dia. This treatment raises the load at which plastic stretching in tension becomes appreciable from 60 to about 130 lb., and hence enables a greater back-pull to be applied. The maximum back-pull used was 122.5 lb., and this pull caused the dia. of the 0.0610 in. dia. wire to decrease by about 0.0001 in. With smaller amounts of back-pull no decrease in dia. could be detected with a micrometer.

The experimental results for castor oil or soap *B* as lubricants are shown in Figs. 16–19. In order to conserve space only the die load, F , has been plotted against back-pull, Q , and it must be remembered that the drawing load, P , equals $F + Q$.

Most of the results have been repeated, and with the soap all the check results exhibit the same curvature and are almost parallel to the curves shown, but there may be a shift of $\pm 2\%$ on the ordinate scale.

The shape and slope of the curves given for castor oil, however, were rather less reproducible, and will not, therefore, be used in calculating μ ; they are included for comparison with the results on soap *B*.

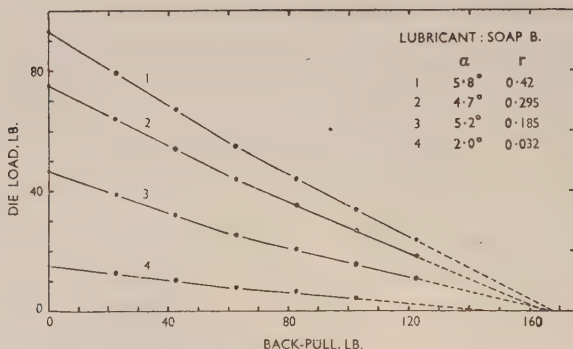


FIG. 17.—Influence of Reduction of Area on Die Load/Back-Pull Curves.

It will be noticed that the relationship between F and Q is in no case *strictly* linear. In all the graphs, b (defined as $-\frac{dF}{dQ}$) decreases

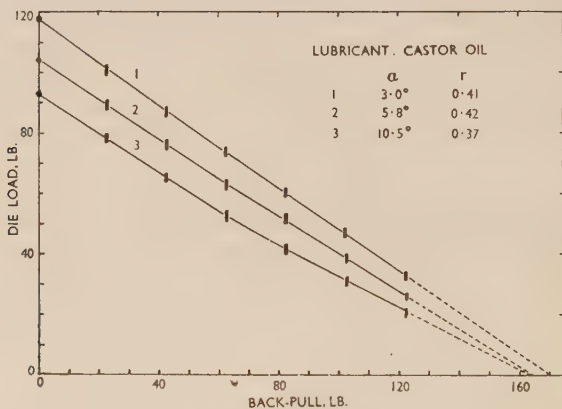


FIG. 18.—Influence of Die-Angle on Die Load/Back-Pull Curves.

with increasing Q , and although this effect is small, it is unmistakable and not caused by experimental errors.

The temperature plays an important part in back-pull experiments, because the amount of back-pull affects the die-wire pressure and hence

also the frictional loss and temperature. With a drawing speed of 3.5 ft./min., however, the die temperature never increased by more than 15° C., so that this complication was not serious. To reduce temperature variations in each experiment to a minimum, the wire was drawn without back-pull until the die temperature (and drawing load) became

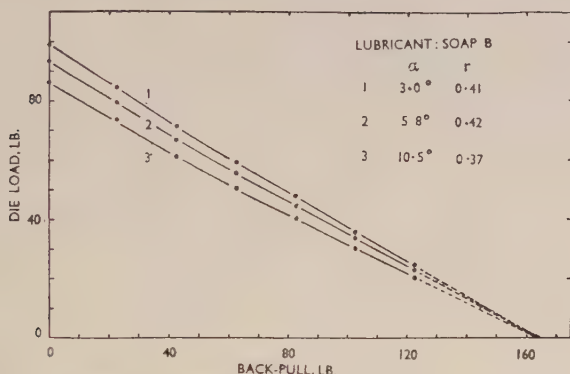


FIG. 19.—Influence of Die-Angle on Die Load/Back-Pull Curves.

constant, and different amounts of back-pull were then applied in random succession for short periods of time, two or three readings being taken for each value of the back-pull.

From these graphs, calculations of μ have been made, using the equations of MacLellan (13) and Hill (14), and the results, for soap B, are given in Table IV. In these calculations, average values of b have

TABLE IV.—Effect of r and α on μ in Back-Pull Experiments, Using Soap B.

Reduction of Area, r	Die-Angle, α	Average Back-Pull b	μ^*		Light Back-Pull b	Heavy Back-Pull b
			MacLellan	Hill		
0.032	2°	0.10	0.08	0.07	0.12	0.08
0.185	5.2°	0.29	0.061	0.052	0.34	0.24
0.30	4.7°	0.46	0.061	0.044	0.50	0.43
0.42	5.8°	0.58	0.060	0.039	0.62	0.54
0.41	3.0°	0.62	0.044	0.027	0.66	0.58
0.405	4.2°	0.59	0.053	0.034	0.63	0.54
0.42	5.8°	0.58	0.060	0.039	0.62	0.54
0.37	10.5°	0.54	0.12	0.085	0.58	0.49

* The values of μ believed to be the most reliable are set in heavy type.

been used. In the table, values of b are shown for light and heavy back-pull, which illustrate the total change in the slope of the F/Q curves.

These results may be compared with those in Table I, and the agreement between the values of μ obtained by the two methods is surprisingly good.

(c) *Effect of Interfacial Pressure.*

It has been mentioned that an increase in back-pull causes the interfacial pressure between the wire and the die to decrease. Now it is implied in equations (13) and (14) that μ remains constant when the back-pull, and hence the pressure, is varied, although previous experiments have shown that it is rare for μ to remain constant when any

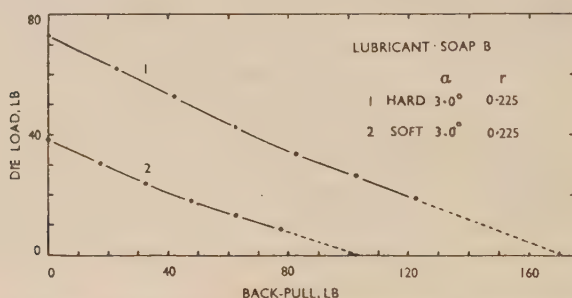


FIG. 20.—Influence of Interfacial Pressure on Die Load/Back-Pull Curves.

important variable is altered. It seemed possible, therefore, that the non-linear relationship between the die load and the back-pull was due to a variation in the value of μ caused by this variation of the pressure.

It is not easy to devise experiments to examine the effect of interfacial pressure on μ whilst keeping all the other variables constant. The method which was eventually used was to carry out back-pull experiments with soft, annealed wire and also with hard-drawn wire under the same conditions. The interfacial pressures will throughout be much greater with the hard-drawn wire, but it should be remembered that in both cases back-pull causes the actual pressure to decrease.

If μ is independent of the pressure, b should be the same for both hard and soft wires. One of the graphs obtained by this procedure is shown in Fig. 20. The initial diameter of the wire used was 0.0530 in., the "soft" wire being prepared by drawing the original wire to 0.055 in. and then annealing it; followed by etching to remove the scale, and rubbing with fine-grade emery paper to remove the thin, copper-rich surface layer. After wiping the surface to remove polishing debris the

wire was sized by drawing to 0.0530 in. dia. The hard wire was treated in the same way, except that the annealing operation was omitted. The surfaces of the hard and soft wires were thus identical, and in each case the finish was very good.

The results tabulated in Table V provide clear evidence that μ does increase as the pressure rises.

TABLE V.—*Effect of Interfacial Pressure on μ , Using Soap B.*

Reduction of Area, r	Die-Angle, α	Condition of Wire	Average Back-Pull, b	μ^*		Light Back-Pull, b	Heavy Back-Pull, b
				MacLellan	Hill		
0.22	3.0°	Hard	0.45	0.073	0.055	0.50	0.38
		Soft	0.38	0.048	0.038	0.44	0.32
0.23	5.5°	Hard	0.39	0.087	0.067	0.43	0.35
		Soft	0.36	0.069	0.054	0.40	0.32

* The values of μ believed to be the most reliable are set in heavy type.

(d) *Effect of Drawing Speed and Temperature.*

It has been shown by Thompson and his co-workers^{19, 20} that the drawing load will decrease at higher temperature if the temperature is raised, or at low drawing speeds if this speed is decreased. This suggests, but does not in itself prove, that the coefficient of friction is affected by these variables. An investigation of the effect of speed and temperature on μ must be carried out at low drawing speeds, since at high speeds the actual temperature at the die/wire interface is a matter for speculation, and severe temperature gradients are set up.

In these experiments the die was heated in a small resistance tube furnace, the temperature being measured by a thermocouple inserted into a hole in the brass casing of the die. During drawing the wire became warm at a distance of about 2 in. from the die. Prolonged heating of the wire before entering the die was avoided for fear of changes in the lubricating films, and so in the coefficient of friction.

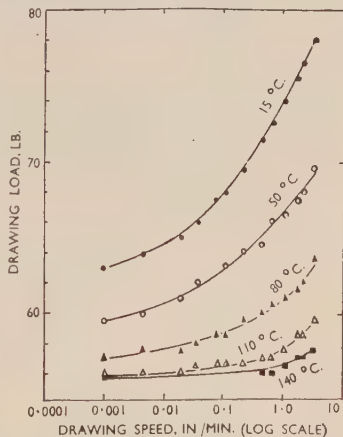


FIG. 21.—*Effect of Drawing Speed and Temperature on Drawing Load.*

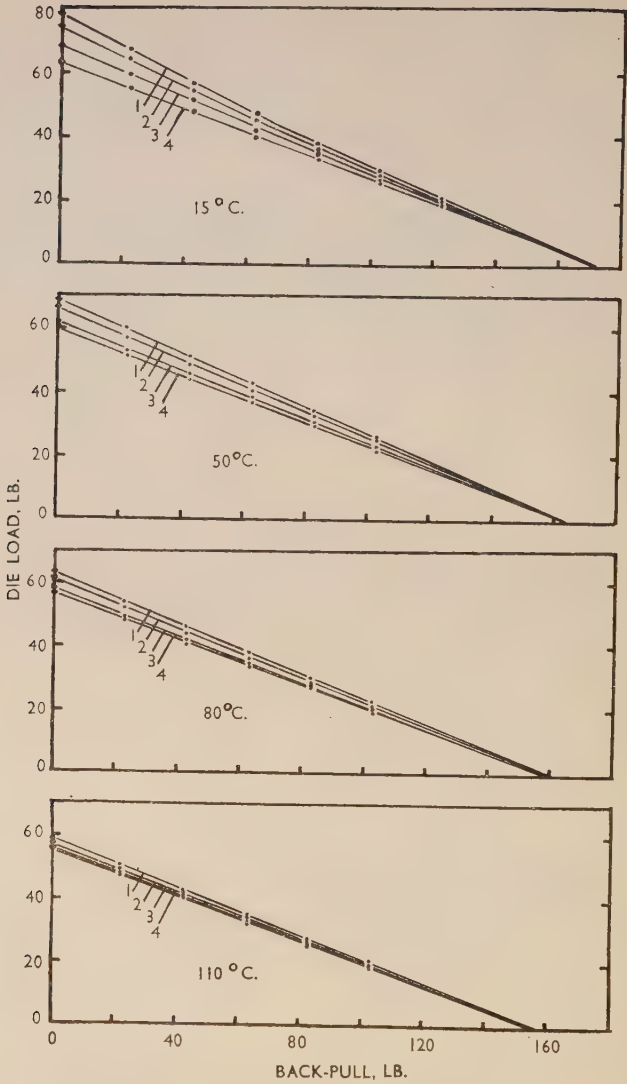


FIG. 22.—Effect of Drawing Speed and Temperature on Die Load/Back-Pull Curves.

Reduction of area $r = 0.335$. Die-angle = 4.1° . Lubricant: Soap C.

KEY.

1
2
3
4

Drawing speed, in./min.

3.3
1.1
0.11
0.001

The annealed brass wire was initially drawn from 0.0644 to 0.0610 in. dia. to raise its yield strength. Soap C was the only lubricant used, and only one die was employed. This was without parallel, with an effective die angle of 4.1° , and giving a reduction of area of 34%.

In the first tests the drawing load (without back-pull) was measured for varying speeds and temperatures. With two independent variables the results can be plotted in a number of ways, but for the present purpose it was convenient to plot the drawing load against the logarithm of the drawing speed, for various temperatures (Fig. 21).

A series of back-pull tests was then carried out with the results shown in Fig. 22. The values of μ derived from the average slope of these curves, using MacLellan's equation, are plotted in Fig. 23. It will be seen first that both drawing speed and temperature have a marked influence on μ , and secondly that, with *very* low drawing speeds, μ is surprisingly small.

An interesting point about these and the previous die load/back-pull graphs is that when the curves are extrapolated to meet the abscissa, the point of intersection corresponds quite closely to the load required to stretch the wire to the same diameter in tension, or to the breaking load, if the wire has been drawn beyond the diameter at which necking in tension begins. This is not a general law, but only an empirical relationship which happens to be true in the present results. The factors influencing the relationship are complex and it is not proposed to discuss them here.

Referring again to the curves in Fig. 22, it will be seen that at each temperature the curves for the different speeds tend to converge to a point on the abscissa, additional evidence for the belief that the stress/strain properties of the brass wire are insensitive to the rate of straining. On the other hand these points of convergence decrease with increasing temperature. The work of deformation decreases as the temperature is raised, and the effect of this can be seen by comparing Fig. 21 with Fig. 23. In Fig. 21 the frictional loss and the work of deformation in drawing are varying simultaneously, and together they account for the shape of the curves. In Fig. 23 the variation of the coefficient of friction under the same conditions is shown.

It will be noticed that in Fig. 22 the majority of the F/Q curves are

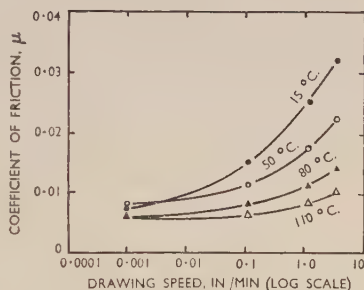


FIG. 23.—Effect of Drawing Speed and Temperature on μ .

strictly linear. In only two curves does b decrease when Q is increased, these being curves for the highest drawing speeds at room temperature, and corresponding to the highest values of μ .

Some experiments were carried out to find the effect of drawing speed when using liquid lubricants. Back-pull was not applied, and μ was calculated from Davis and Dokos's equation. It was found that μ decreased with the drawing speed, but the effect was not as marked as with the soap lubricant. When the speed was decreased, a critical drawing speed and value of μ were found, below which "stick-slip" friction occurred; at this speed the lubricating film is ruptured, causing localized seizure.

Within the range of speeds investigated, μ increased when the speed was increased, but it seemed probable that at still higher speeds this trend might be countered to some extent by an increase in the thickness of the lubricating film, especially with the viscous soap lubricants. In support of this view, Fig. 27 (Plate L) shows the surfaces of two wires which were drawn at different speeds. That drawn at approximately 1000 ft./min. was covered with a thick layer of soap which can be seen in the photograph, the thickness of the film being of the order of 0.001 in. It is apparent that the film is not continuous, but it may well have broken up in this manner on emerging from the die. In the cases of the other wire, drawn at 3.5 ft./min., the soap film was too thin to be visible.

(e) *Discussion.*

It has been concluded that the most accurate theory of wire-drawing in the present experimental circumstances is probably that due to Davis and Dokos, and if this be true, their theory must also provide the most accurate equation for back-pull drawing, since all the basic principles remain the same. It so happens that MacLellan's extension of Sachs's theory gives the same result as does that of Davis and Dokos, because strain-hardening does not affect the back-pull equation for b . It is, therefore, believed that the most accurate values of μ are those calculated from MacLellan's equation (13).

Possible sources of error which may affect the shape of the back-pull curves will now be examined.

At first it was hoped that this method of deriving μ would not be subject to errors from redundant strain, but further consideration shows that this is not true. If there is a large amount of redundant strain in drawing, the application of back-pull will tend to make deformation more homogeneous, since the axial tension increases and the interfacial pressure decreases. Eventually, if the back-pull is made

sufficiently large, the pressure on the die wall vanishes and the wire is stretched in simple tension.

Some work by Simons²¹ (reviewed by Wistreich²²) shows that the deformation does in fact become more homogeneous when back-pull is applied. Simons found that the hardness of drawn wire (33% reduction of area and "14° die-angle") was slightly greater at the centre than at the surface, and that this difference of hardness decreased when the wire was drawn with back-pull. When the wire was drawn with heavy back-pull the hardness became essentially uniform.

There is little doubt that if there is redundant strain it will decrease when back-pull is applied, the effect being to increase b , and make the derived values of μ too high. This can be demonstrated by using Hill and Tupper's complete equation (17), and assuming, for simplicity, that

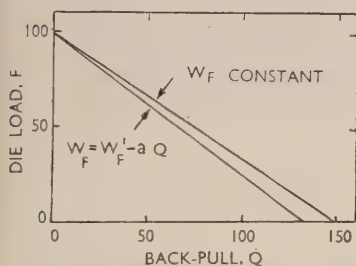


FIG. 24.—Illustrating Effect of Redundant Work on the F/Q Curve.

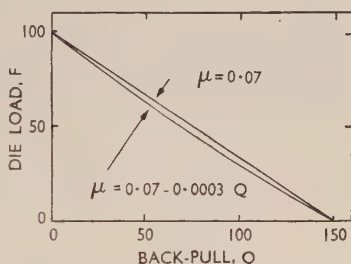


FIG. 25.—Illustrating Effect of Variations of μ on the F/Q Curve.

the decrease in redundant strain causes W_F to decrease as a linear function of Q :

$$W_F = W_{F1} - aQ$$

When this is substituted in (17), an F/Q relationship of the form shown in Fig. 24 is obtained.

The most accurate results in Table IV are those in which redundant strain is very small, or absent, and these results are shown in heavy type.

Experimental evidence has been given to show that μ decreases when the normal pressure on the die wall decreases, i.e. when back-pull is applied. It is important to find what effect this will have on the form of the F/Q relationship and on the derived values of μ . Assuming that μ decreases linearly with increasing Q , i.e.:

$$\mu = \mu_1 - gQ,$$

and substituting this in Davis and Dokos's complete equation (16), a theoretical relationship is obtained between F and Q , the form of which is illustrated by Fig. 25. In plotting this graph, the various

terms in the equation have been given arbitrary, but typical, values, and it should be noted that the constants μ_1 and g have been chosen so that μ does not become negative in the range of Q considered (when $Q = 0$, $\mu = 0.07$; and when $F = 0$, $\mu = 0.025$).

It will be seen from Fig. 25 that the factor b decreases when Q increases. The curve coincides with the straight line for $\mu = 0.07$ (constant) when $Q = 0$ and when $F = 0$, and although μ is made to decrease almost to zero, yet the curve never deviates far from the straight line for $\mu = 0.07$. If the linear equation for μ is substituted in Sachs's complete equation (15), or Hill and Tupper's complete equation (17), the resulting F/Q relationships

have exactly the same characteristics as this curve. The similarity between the curve in Fig. 25 and the experimental curves is very marked, and there can be little doubt that the non-rectilinear relationship between F and Q is due to μ decreasing when the back-pull is increased.

In Fig. 25 the average value of the slope b over the total range from $Q = 0$ to $F = 0$ is the same as that when μ is constant, i.e. average values of b can be used to derive μ for drawing without back-pull. In practice the whole range cannot be covered because the back-pull must not be allowed to deform the wire, and it will be seen that this makes the average slope (b) too high. As

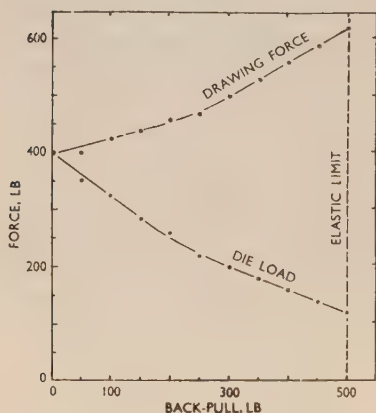


FIG. 26.— F/Q Curve. According to L. Simons.²¹

Material: 0.44% carbon patented steel wire, 0.098 in. dia.

Reduction of area $r = 0.333$. Die: "14° angle, 50% length of bearing."

Lubricant: dry soap. Drawing speed: "very slow."

a result, the derived values of μ in Tables IV and V will be slightly larger than the true values for drawing without back-pull.

It is widely believed that the relationship between F and Q is strictly linear, and it is now intended very briefly to review previous work on this subject and consider whether the present results are incompatible.

Stringfellow²³ contended that the slope b decreased with increasing back-pull, but in support of this view he provides only one, rather irregular graph, and gives no experimental details. Simons²¹ carried out a careful experiment, using a low-speed, hand-driven bench, and the graph he obtained is similar to that obtained from the present results (Fig. 26). Simons did not comment on the shape of this graph,

and later reviewers have not mentioned it. The F/Q graphs given by Lueg and Pomp²⁴ are practically rectilinear. These authors used relatively high drawing speeds, and demonstrated that there was a marked fall in temperature as the back-pull increased due to the decrease in frictional losses. This fall in temperature will tend to cause μ to rise, and this will oppose the tendency for b to decrease when Q is increased. In the present experiments the drawing was effectively isothermal.

In his review of back-pull drawing Wistreich²² quotes unpublished results by Heselwood, who used a drawing speed of 2 ft./min., and found that straight lines fitted all his results. The maximum back-pull used by Heselwood was, however, relatively low, and had it not been higher in the present experiments it would have been impossible to detect any curvature. The ratio of maximum back-pull to the drawing force without back-pull, varied from 1 : 1 to 1 : 2 in Heselwood's experiments, whereas in the present work the ratio varied from 7 : 1 to 1 : 1. MacLellan⁶ believes that any deviation from linearity is due to inadequate experimental control, but gives no reason for this belief, nor any results to justify it.

In the present experiments a linear relationship between F and Q was obtained when the drawing speed was very low. These results are in complete agreement with the contention that change of slope is due to a decrease in μ ; in these rectilinear curves μ is already so small that any further decrease would cause no detectable change of slope.

In the original back-pull experiments Thompson¹⁸ used a very low drawing speed and a very good lubricant. He obtained straight-line graphs, and recently μ has been derived from these graphs and found to be very small. This agrees well with the present results. It is interesting to note, however, that the accuracy of his results has been questioned on the very grounds that the values of μ derived were thought to be too small to be true.

IV.—EXAMINATION AND INTERPRETATION OF RESULTS.

In previous sections the accuracy of the values of μ obtained have been discussed, and the curves in Fig. 23 and the results given in heavy type in Tables I-V, are shown, it is believed, to be reliable, both in relation to each other, and also, though to a lesser extent, in absolute accuracy. In the latter respect, however, they are probably slightly too high, but it is considered that this error will be less than 30%. It now remains to examine and interpret these results.

Friction is usually divided into three categories, dry, boundary, and hydrodynamic (or fluid-film); and it has generally been believed

that in wire drawing the friction is of the boundary type. Boundary lubrication is found when the pressures are too high, or the speeds too low, for the maintenance of a stable, hydrodynamic film of lubricant. The surfaces are then covered by a thin adsorbed film of lubricant which is only a few molecules thick, and may even be monomolecular, and the values of μ obtained usually fall within the range 0.15–0.05. Lubricants containing long-chain hydrocarbon molecules with a polar group at one end, such as the fatty acids, give the lowest values of μ under conditions of boundary lubrication. In the present experiments, the good lubricating properties of the soaps, the castor oil, and probably the R.O.D. emulsion, are mainly due to their fatty-acid content.

Until recently it was thought that boundary lubrication was quite distinct from hydrodynamic lubrication, it being held that in the former μ was independent of the sliding speed and of the interfacial pressure. However, in 1940 Beeck, Givens, and Smith²⁵ showed that there is a transitional region, which they termed "quasi-hydrodynamic", between boundary and hydrodynamic conditions, in which μ decreases as the speed is raised. Subsequent work has confirmed and ramified this view, but the whole subject is at the moment in a state of flux. For further information reference may be made to a review published by Bowden, Gregory, and Tabor²⁶ in 1945; and a more recent one by Burwell and Strang.²⁷

The coefficients of friction obtained with a drawing speed of 3.5 ft./min. agree quite well with published work on boundary lubrication. Three values of μ for castor oil have been noticed in the literature; in two cases $\mu = 0.10$ and in the other $\mu = 0.05$. In the present work μ varied between 0.069 and 0.081.

Francis²⁸ tested a number of wire-drawing lubricants in a friction-testing instrument with results similar to the values in Table II, including the following figures :

Lubricant					μ
Soap B	0.067
R.O.D. emulsion	0.07
Castor oil	0.10

He believed that the soaps provided boundary lubrication, but it is interesting to note that he found some "slip-back" in his friction machine when the motor was stopped, and suggests that this "may be because the coefficient of friction falls with decreasing speed".

With the exception of this work by Francis, no published results have been found on the coefficient of friction of wire-drawing soaps. There are, of course, a number of papers in which μ has been estimated from wire-drawing experiments, but no comprehensive investigation has

been made, and for one reason or another many of these estimates are open to suspicion.

The present results will now be considered by themselves.

The surface finish of the die had a marked influence on μ when using castor oil (Table III), as is to be expected with boundary lubrication. A rough finish leaves a large number of high spots on the surface where there will be heavy stress concentrations, leading to rupture of the boundary film, and so to seizure.

With soap *B*, however, the drawing load, and μ , increased only very slightly on rough-lapping the die. The explanation for this behaviour seems to be that a relatively thick film is formed, of a depth greater than that of the scratches, and hence providing hydrodynamic (or quasi-hydrodynamic) lubrication. It should be noted, however, that the scratches were transverse, or circumferential, and that it would be very difficult for the viscous soap trapped in these grooves to escape; whereas longitudinal scratches would be of less assistance in maintaining a thick film.

In discussing the results obtained with wire-drawing soaps, it is convenient to make use of the approximate relationship for hydrodynamic lubrication²⁸:

$$f = H \frac{\eta v}{t},$$

where f is the frictional force per unit area of contact between the surfaces, H is a constant, η the viscosity, v the relative velocity, and t the film thickness; and since $\mu = f/p$, where p is the pressure (per unit area) between the surfaces:

$$\mu = H \frac{\eta v}{tp} \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

In addition, the film thickness t is also a function of the three independent variables η , v , and p . The hydrodynamic film is maintained by "viscous drag" or "wedge" action, and the film thickness tends to be increased by an increase in η or v , but diminished by an increase in p .

It was found that a decrease in the pressure between the wire and the die caused μ to decrease (Table V), and it therefore follows from equation (18) that tp increased, and so the film thickness must have increased considerably.

The initial stage of deformation, when the wire first comes into contact with the die, is very important in determining the thickness of the lubricating film and hence the coefficient of friction. Just before the wire touches the die the lubricant is piled up round the wire, and

only a small proportion of this lubricant will be drawn by "wedge" action into the deformation zone. However, once the film is actually in the zone it will be difficult for it to escape, and it may be expected that practically the same thickness of lubricant will be maintained throughout the die. (There will of course be a slight mechanical reduction in film thickness because the surface area of the drawn wire is greater than that of the original wire.) The thickness of the lubricating film which is first admitted will depend on a number of variables, such as the die-angle, the lubricant, and the initial pressure between the die and the wire.

In the experiments in which the reduction of area was varied, these factors were all approximately constant, and since the same annealed wire was used in each experiment, the initial pressures would be constant. One would, therefore, expect the film thickness to be the same for each reduction of area.

The reduction of area has little or no influence on μ , and since η , v , and t in equation (18) are constant, it follows that the average interfacial pressure p over the whole contact area must have been approximately the same for each reduction of area. Evidence from other directions supports the view that the average pressure is almost constant, except, however, when the drawing load approaches the breaking load of the wire, when the average pressure decreases slightly. For instance, if the average pressure is constant it can be shown from simple considerations that the relationship between drawing load and reduction of area should be linear, for dies without parallel extensions. When the results in Fig. 9 are plotted in this way it is found that the relationship is almost linear within the range 0–50% reduction of area.

A distinct tendency was, however, found for μ to decrease with decreasing die-angle. (Tables I, II, and IV.) The most probable explanation is that the wedge effect exercises more influence and leads to a thicker film of lubricant when the die-angle is small. From Table II it will be seen that this effect of the die-angle is greatest with the best lubricants. When the die-angle is increased from 3.0° to 6.1° , μ is almost doubled with soap *B*, but with Hypoid 90 and Oil-Dag there is practically no change. The viscosity of the lubricant must play a large part. A viscous lubricant, such as a soap, which adheres well to the wire, will be more easily drawn into the die and less easily forced backwards than a fluid lubricant.

The effect of the drawing speed on μ presents a more complex problem, but the fact that the speed does have a marked influence on μ confirms the view that soap lubrication is more hydrodynamic than boundary in nature.

In the experiments with soap C (Fig. 22) the only factor varied at each temperature was the drawing speed, and it therefore follows, from equation (18), that the film thickness :

$$t = J \frac{v}{\mu},$$

where J is a constant. This equation can be used to calculate the approximate variation of film thickness with drawing speed from the curves in Fig. 23. At room temperature, with a drawing speed, v , of 3.3 in./min., $t = 100J$; when $v = 0.1$ in./min., $t = 6.7J$; and when $v = 0.001$ in./min., $t = 0.14J$.

Even if equation (18) is not ideally applicable, these figures leave no doubt that there is a marked decrease in the thickness of the film when the speed is decreased. Conversely, it is not surprising that when the speed was raised to 1000 ft./min. the film became so thick as to be visible. It is concluded that the film thickness decreases when the speed is lowered, but, except at the lowest speeds investigated, the ratio v/t also decreases, and hence μ is reduced.

The variation of μ with drawing speed was much less with the liquid lubricants than with soap, but it was still sufficient to show the existence of wedge effect and a certain amount of hydrodynamic tendency. At some critical speed and value of μ , however, "stick-slip" friction occurred. At this point it is probable that the film becomes too thin to separate the surfaces effectively, and localized seizure takes place. The drawing load then increases until the wire is suddenly drawn again, a thicker film is momentarily formed, the speed again falls rapidly, and the cycle is repeated. Stick-slip friction was also found with soap lubricants at temperatures above 110° C. but not at lower temperatures. This is probably due to a combination of factors; the moisture in the soap will form steam and tend to disrupt the film, the viscosity of the lubricant will be reduced, the lateral attractive forces between the molecules in the primary adsorbed film will become weaker, and the film will, therefore, be more easily ruptured.

An increase in temperature causes the viscosity of the lubricant to decrease, and at most speeds this resulted in a fall in value of μ (Fig. 23), showing that the ratio η/t in equation (18) had decreased. However, at the lowest drawing speeds the temperature, within the range investigated, had no measurable influence on μ . It is at first sight difficult to believe that at a temperature of 110° C. and with a drawing speed of 0.001 in./min., a stable hydrodynamic film can be supported, but the value of μ was so low (0.007) that no other explanation can be entertained. It follows then that at these very low speeds the ratio η/t must

remain approximately constant when the temperature is raised to about 120° C., but at this temperature the film suddenly breaks down and stick-slip friction begins.

At high drawing speeds both the speed and the heat generated in the die will influence the coefficient of friction, and, therefore, the drawing load; whilst, in addition, the heat generated in the die will also affect the work of deformation. Francis and Thompson²⁹ have shown that the drawing load remains approximately constant when the speed is varied over the range 30–600 ft./min. It follows, therefore, that the factors mentioned above must approximately counterbalance each other, and that in all probability the coefficient of friction increases slightly when the speed is increased in this range.

To sum up, these experiments suggest that the lubrication in wire-drawing is normally quasi-hydrodynamic in nature under a variety of conditions. The experiments on the effect of surface finish and on the effect of velocity and pressure show that the soap lubricants provide a film which is thicker and more nearly hydrodynamic in its behaviour than do the liquid lubricants. The worst lubricants were those which showed the least hydrodynamic tendencies.

The curves in Fig. 23 are probably the most interesting from the frictional point of view, showing a marked decrease in μ when the sliding speed was reduced, whereas the opposite effect is usually described in published work on quasi-hydrodynamic friction. Quasi-hydrodynamic friction has previously been noted in experiments with friction-testing machines, but this is probably the first time that it has been found in an industrial process. These results are in complete agreement with the statement by Beeck, Givens, and Smith²⁵ that “long-chain polar compounds act primarily by inducing the wedging effect and not by giving direct protection to the surface”.

V.—CONCLUSIONS.

The Stress/Strain Curves of Brass Wire.

(1) A reasonably accurate complete true stress/true strain curve beyond the necking point in tension is provided by the envelope of a series of true stress/true strain curves for drawn wires. These wires are of different diameters, and must be drawn through dies with small apical angles. The individual curves have their origin on the strain axis at the point corresponding to their diameter.

(2) The stress/strain curve of the 65 : 35 annealed brass wire used in this work was, for practical purposes, unaffected by variations in the rate of straining.

(3) A room-temperature ageing effect has been noticed in the 65 : 35 drawn brass wire under certain conditions. The 0.2% proof stress, for instance, decreased when the wire was aged.

The Extent of the Frictional Loss.

(4) A heavy pass is more economical in the total work done than are a series of light passes which give the same final diameter.

(5) The ratio $\frac{\text{work wasted in friction}}{\text{total work done}}$ decreases as the reduction of area is increased.

(6) The ratio $\frac{\text{work done in the parallel zone of the die}}{\text{total work done}}$ decreases as the reduction of area is increased, and eventually becomes zero when the drawing load approaches the breaking load of the wire.

Theories of Wire-Drawing.

(7) When these theories are used to estimate μ , redundant work (due to internal shear strains which do not contribute directly towards the reduction of area in drawing) should be made very small by using small die-angles and large reductions of area.

(8) The three wire-drawing theories due to Sachs, to Davis and Dokos, and to Hill and Tupper, respectively, all agree that when friction and redundant work are zero, the work done in drawing is equal to the work done in simple tensile stretching.

(9) Sachs's equation becomes very inaccurate, and eventually fails completely, when the drawing stress becomes greater than the "mean yield stress", Y_m . Even when the drawing stress is smaller than Y_m , Sachs's equation gives results which are appreciably different from those derived from that of Davis and Dokos, showing that the assumption of a constant mean yield stress in his theory introduces appreciable errors.

(10) If μ is calculated from the different theories, that of Sachs gives the largest value of μ , that of Davis and Dokos a lower value, and Hill and Tupper's theory the smallest.

(11) The elastic term which Davis and Dokos add to their equation is inaccurate, and should be omitted.

(12) When this elastic term is neglected, and when redundant work is small or zero, Davis and Dokos's equation appears to be more accurate than the equations of Sachs or of Hill and Tupper, and can be used to calculate reliable values of μ .

(13) The various sources of error in Davis and Dokos's equation are

small, and all tend to make the calculated values of μ too large. It is believed that in the present work this error is of the order of 0.01.

(14) The theories of wire drawing involve assumptions regarding both the work of deformation and strain-hardening, which the back-pull equations avoid. The fact that the two methods of deriving μ gave very similar results shows that these assumptions are not seriously in error.

Wire-Drawing with Back-Pull.

(15) MacLellan's equation for back-pull drawing is believed to be more accurate than Hill's equation, when redundant work is small.

(16) The amount of redundant work will decrease when back-pull is applied. This will make the slope b of the die load/back-pull curves too large, and hence the derived values of μ will again be too high. Redundant work should, therefore, be avoided by making the die-angles small and the reduction of area large.

(17) The slope b of the die load/back-pull curves was found to decrease with increasing back-pull. This deviation from linearity is small, and is due to μ decreasing as the back-pull is increased.

(18) The average value of b is, therefore, slightly too high, and hence the derived value of μ will be slightly larger than the true value for drawing without back-pull.

(19) When μ is already very small this effect is proportionately small and the die load/back-pull graph becomes a straight line. Back-pull experiments provide the most accurate method of deriving μ , when μ is small.

*Lubrication and the Coefficient of Friction.**

(20) The lubricants which have been used are given below in order of merit, together with the range of values of μ that have been obtained :

<i>Lubricant</i>	μ
Soap B	0.033-0.061
R.O.D. emulsion	0.064-0.077
Castor oil	0.069-0.081
Oil Dag	0.088-0.096
Hypoid 90	0.10 -0.11

(Drawing speed 3.5 ft./min.; well-polished Widia dies, die semi-angles : 2.8°-6.1°; reductions of area : 27-48%.)

(21) The percentage reduction of area does not affect μ .

(22) With the better lubricants μ decreases when the die-angle is reduced, but with the poorer lubricants the die-angle has little or no influence.

* These conclusions refer to the drawing of annealed brass wire through carbide dies.

(23) With good soap lubricants the surface finish of the die has little effect on μ , but with the liquid lubricants the surface finish has a marked influence.

(24) With good lubricants μ decreases when the interfacial pressure is reduced.

(25) With good soap lubricants μ decreases continuously as the speed is reduced from 3.3 to 0.001 in./min. With liquid lubricants μ decreases when the speed is reduced from 3.5 ft./min., but at some critical speed, which is quite low, there is again an increase in μ .

(26) With good soap lubricants, the lubricating film tends to become much thicker when the speed is increased to the region of 1000 ft./min.

(27) With good soap lubricants, μ decreases when the temperature is raised up to 120° C., except when the drawing speed is less than 0.01 in./min.

(28) The wire-drawing soaps provide a relatively thick film of lubricant which behaves hydrodynamically. With liquid lubricants the film is thinner and nearer to the boundary state, but the best liquid lubricants show some hydrodynamic tendencies.

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FUNDAMENTAL ASPECTS OF THE COLD 1286 WORKING OF METALS.*

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SYNOPSIS.

Reference is made to the nature of the metallic state and metallic cohesion in terms of the electron theory of metals, and a brief outline is given of the several mechanisms involved in plastic deformation. These include crystallographic slip, twinning, and kinking, and a sheer mechanism to which particular attention is drawn because of its importance in many metal-fabrication processes. The influence of plastic deformation on structure is described with special reference to the development of preferred orientation in view of its technological significance, while the effect of deformation on the fine structure as revealed primarily by X-ray diffraction studies is considered in terms of the dislocation theory. The relation of work-hardening and plasticity to the structural changes brought about by cold working is also discussed.

I.—INTRODUCTION.

THIS contribution to the Symposium is different in character from the other four for, while it is concerned, as they are, with the cold working of metals, it deals with the nature of the internal or structural changes involved in cold plastic deformation and not with technological aspects of the subject. Our knowledge of the fundamentals of plastic deformation is still far from complete, but it has been enriched at an increasing rate in recent years, and the primary purpose of this paper is to provide a background study, in so far as it can be made in the light of existing knowledge and concepts, of the mechanism of the changes which take place when metals and alloys are plastically deformed in the cold state, as they are in the various manufacturing operations covered by the other papers contributed to this Symposium.

For a proper appreciation of metallic properties it is first necessary to refer to the electron theory¹ of metals since this accounts very satisfactorily for the electrical, magnetic, and thermal properties of metals, for many facts associated with the constitution of alloys, and for the nature of the cohesive or binding forces of metals.

According to the electron theory, the valency electrons of a metal in the solid state, or at least a definite proportion of them, are not

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associated with particular atoms. A metallic crystal is thus considered to be an assembly of positively charged ions in a cloud of free electrons, the positive ions being held together in positions of minimum energy by the opposing forces of electrostatic attraction between their positive charges and the negative charges of the electrons, and repulsion between their own positive charges.

On the basis of such a conception it is possible to calculate the lattice constants and compressibilities of metals, and, in fact, such calculations made with respect to the alkali metals lithium and sodium, which have the simplest atomic structures, have yielded values agreeing reasonably well with those determined by direct measurement. The atomic packing arrangements of metals in general are also accounted for by the electron theory, particularly the common close-packed, face-centred cubic structure as found in copper, silver, and gold, in which the diameter of the ions is a large proportion of the total interatomic spacing.

The fact that many metals can be deformed to a considerable extent without fracture, by slip in directions of closest atomic packing and generally upon planes of densest packing, is also explained by the electron theory, since the process can take place by relative movement of the positive ions while they still remain within the electrostatic fields of force associated with the electron cloud. It is in this latter respect that deformation of metals differs from that of typical ionic compounds in which negative as well as positive ions occupy fixed positions within the lattice.

The electron theory has not, however, provided a satisfactory explanation of the facts that metals yield and fracture at very much smaller stresses than a theoretical consideration of internal electrostatic forces would suggest, and harden when they are plastically deformed in the cold. Nevertheless, enough information is now available for a picture to be provided of the structural changes associated with deformation, and it is with this aspect of the subject that the paper is chiefly concerned. The structural movements associated with deformation such as slip, shear, and twinning are first considered, then structural changes such as the development of preferred orientation or textures, crystal fragmentation and lattice distortion, and, finally, the relation between these structural conditions and workability.

II.—MECHANISM OF PLASTIC DEFORMATION.

When a piece of wrought metal, a mass of randomly orientated crystals, is plastically deformed in the cold state, that is, when it is subjected to a permanent change in shape by cold working, the total

amount of deformation which it undergoes is made up of the deformation of the individual crystals together with that arising from relative movement of crystals at their common boundaries by a process of viscous flow. Deformation arising from relative movement at grain boundaries constitutes, however, an insignificant part of the total except at very slow rates of strain, as, for example, under creep conditions, and consequently it is not considered further in this discussion.

In normal cold-working operations such as rolling, the individual crystals are each deformed in direct proportion to the amount of deformation of the whole mass of metal. This effect, termed homogeneous deformation, is illustrated by Fig. 1 (Plate LI), which is a composite photograph made up of photomicrographs of three sections parallel to the three principal planes of a copper strip which has been cold rolled with a reduction in thickness of 80%. It was first suggested over fifty years ago by Ewing and Rosenhain² that such deformation in metal crystals occurs by a process of slip within the individual crystals themselves, and since then the mechanism has been studied in very great detail.³ The identification of the planes in which slip takes place in metals with different crystal structures, and a study of the change in direction of these planes during plastic deformation, has helped to explain the difference in behaviour of single and polycrystalline structures and between different metals. It has, furthermore, led to an understanding of the development of textures in cold-worked metals, yielding results of practical value in the production of wrought material either completely free from directional properties or with desired degrees of preferred crystalline orientation, as required for various industrial purposes.

1. *Deformation by Slip.*

(a) *Single Crystals.*

Investigations on single crystals have proved of great help in establishing details of slip mechanism. Many workers sought to prove that single metal crystals deform by slip, from the appearance of slip lines on the surface of extended specimens. The possibility remained, nevertheless, that these lines might be merely a surface effect and not evidence of the existence of slip planes, until Taylor and Elam⁴ demonstrated that it was possible to determine the exact nature of plastic deformation by analysing measurements of six external parameters on a single crystal before and after extension. In this way these authors proved beyond doubt that aluminium single crystals deformed by glide upon {111} planes in $\langle 110 \rangle$ directions, which are the planes and directions of closest atomic packing in face-centred cubic structures. Since

there are four families of $\{111\}$ planes in a single crystal, with three $\langle 110 \rangle$ directions in each, there are twelve slip systems. Slip occurs on the $\{111\}$ plane in which the shear stress is greatest and in the $\langle 110 \rangle$ direction along which the resolved component of this shear stress is at a maximum. These observations have been confirmed with other metals and, in fact, in single crystals of every face-centred cubic metal yet examined slip occurs on a $\{111\}$ plane in a $\langle 110 \rangle$ direction.

Furthermore, it has been established that during the deformation of face-centred cubic metals the operative slip plane rotates about an axis perpendicular to both slip direction and stress axis, so that it is then possible for a second slip system to become oriented more favourably for further slip, and deformation continues simultaneously or alternately upon the two systems. These findings explain, in part, the ease with which most pure face-centred cubic metals can be plastically deformed in the cold state.

In all body-centred cubic metals which have been investigated slip occurs in the close-packed $\langle 111 \rangle$ directions. The slip planes, however, vary from one metal to another, being $\{112\}$ in molybdenum, tungsten, and sodium, $\{110\}$ in α iron-silicon alloys and β brass, and $\{123\}$ in potassium. α iron behaves in a different way, since there is no single, well-defined slip plane, slip occurring on $\{110\}$, $\{112\}$, and $\{123\}$ planes, giving rise to the phenomenon known as pencil glide.

In close-packed hexagonal metals also, such as zinc and magnesium, deformation occurs by slip upon the plane of densest atomic packing, namely, the basal plane (0001), and in the direction of closest atomic packing, i.e. a $\langle 1120 \rangle$ direction in that plane. The particular crystal direction in which slip occurs is, as with face-centred cubic crystals, the one along which the resolved shear-stress component is greatest. There is, however, in close-packed hexagonal crystals only one family of basal planes, and when the deforming stress is applied in directions parallel or perpendicular to these planes, then the resolved shear on the slip plane is zero, and under these conditions slip cannot take place and the specimen fractures. This is illustrated in Fig. 2 (Plate LI), which shows fractures in large crystals of pure zinc rolled with a 10% reduction in thickness.

There is evidence that at higher temperatures slip planes other than those mentioned above are involved, but the slip direction remains unchanged. Thus, it has been demonstrated³ that at 450° C. the slip plane for a number of face-centred cubic metals is $\{100\}$, while at 225° C. the close-packed hexagonal metals, magnesium, zinc, and cadmium, slip on planes $\{1011\}$ or $\{1012\}$. These facts suggest that there is a critical temperature for each metal above which different slip planes

become operative, and this may account for the fact that some close-packed hexagonal metals can be much more readily worked above certain temperatures, since slip may then occur on any one of twelve families of planes instead of one. For zinc and cadmium this temperature is probably little, if at all, above room temperature, but magnesium can be readily deformed only at temperatures exceeding 200° C.

With progressively increasing deformation the number of slip lines appearing on the surface of a deformed single crystal increases, but there appears to be a minimum separation of the lines, depending on the metal and the conditions of strain, which suggests that there is a limit to the possible number of slip planes. Furthermore, there is evidence that the degree of displacement on a given slip plane in the slip direction is also limited, for example, Treuting and Brick ⁵ demonstrated that the minimum separation of slip lines in α brass is of the order of 2000 atomic diameters and the displacement about 700 atomic diameters. If, then, both the number of slip planes and the amount of slip occurring in each plane are limited, the total deformation possible by slip is perforce also limited, and other mechanisms must, therefore, become operative when cold working is carried beyond this point.

(b) *Polycrystalline Metals.*

Because of the difference in lattice orientation between adjacent crystals in polycrystalline metal, the most favourable direction of slip in one crystal differs from that in its neighbours. There is consequently physical obstruction to the normal slip process at crystal boundaries, and each crystal is constrained to deform homogeneously as a part of the whole assembly. As Taylor ⁶ has indicated, six components of strain are sufficient to define uniquely any strain, but when, as in plastic deformation of metals, this occurs entirely by shear without a change in volume, then the number of shear components can be reduced to five. It follows that for completely homogeneous deformation in a polycrystalline, face-centred cubic metal, five of the twelve possible slip systems within each crystal must be operative simultaneously instead of the one particular system corresponding to the maximum resolved shear. The five systems are those by which the strain can be effected with the minimum expenditure of energy and comprise two component shears on each of two slip planes, one on a third, and none on the fourth plane. The fact that slip occurs on three planes within each crystal can be demonstrated micrographically, e.g. in Fig. 3 (Plate LI), which represents the surface of an electropolished 70 : 30

brass strip of medium grain-size which has been stretched 5%, and in which the three families of slip lines are clearly seen in one of the crystals.

Homogeneous deformation by slip is possible in pure body-centred cubic metals because of the variety of slip systems available in each individual crystal. Slip in body-centred cubic alloys may, however, be restricted by factors such as structural transformation which influence cold workability, as, for example, in the β copper alloys.

The restriction of slip in close-packed hexagonal metals to a single family of planes has the result that polycrystalline specimens cannot deform homogeneously by slip alone. There are, however, other mechanisms of deformation discussed in the following section which facilitate cold working in metals and alloys of this type.

In operations involving the deformation of a polycrystalline metal with a free surface, crystals near the surface are not fully constrained, and therefore do not deform homogeneously. This gives rise to surface irregularities which, if the crystals are sufficiently large, result in the well-known orange-peel effect. Such surface irregularity is, in fact, visible on the specimen illustrated in Fig. 3.

2. *Other Modes of Deformation.*

(a) *Twinning and Kinking.*

In slip, as described above, deformation occurs by the relative movement of parallel-sided blocks, or slip packets, without any abrupt change in the lattice orientation of the packets themselves. In addition to slip, deformation can take place by twinning and kinking,⁷ involving relatively small atomic movements throughout extensive regions of the stressed crystal, giving rise to a large abrupt change in lattice orientation. In face-centred and body-centred cubic structures, where slip can occur on many planes, the amount of deformation occurring by twinning is small, and kinking has not as yet been observed, but in close-packed hexagonal metals in which, as already mentioned, the possibility of slip is restricted, the amount of deformation which can take place by twinning and kinking is considerable. For example, extensive twinning occurs in zinc during cold rolling and this possibly accounts to some extent for the good workability of the polycrystalline metal. By contrast, twinning does not normally occur during cold rolling of pure magnesium, which fractures after relatively small reductions. There is evidence to suggest, however, that twinning in magnesium is facilitated by alloying with small amounts of various elements such as calcium and lithium, which improve workability.

(b) *Shear.*

It has already been indicated that there is a limit to the amount of deformation that can occur by slip alone, and in the production of wrought metals the deformation generally exceeds this limit, so that a second process must be operative. This conclusion has been confirmed by direct observations made by Adcock⁸ during a study of the cold rolling and recrystallization of cupro-nickel, and by the present authors in similar investigations on both copper⁹ and 70 : 30 brass.¹⁰ This work has demonstrated that when strip thickness is reduced by cold rolling in excess of about 50%, deformation occurs by shear upon planes situated transversely to the rolling direction and inclined to the strip surface, that is to say, on planes related to the direction of the applied stress rather than to the crystal orientation. Shear produced in this manner by heavy cold working is illustrated in Fig. 4 (Plate LII), which is a photomicrograph of a single crystal in a polycrystalline copper strip reduced 80% in thickness by cold rolling, as it appears in a section parallel to the strip surface. The white zigzag band in the centre is a long narrow twin lying in the rolling direction developed at an earlier stage in the rolling, such as is sometimes observed in the coarser crystals. The stepped nature of this twin band and the coincidence of the steps with the transverse surface markings are a clear indication that the metal has deformed by shear on transverse planes subsequent to the twinning.

The shear markings associated with this second mechanism of deformation are less fine and smooth than the slip lines referred to previously, and they are less regularly spaced. Further, while the orientation of slip lines is always related to that of individual crystals, the direction of shear marks is dependent on the directions of the applied deforming stresses. This does not exclude some relation to crystal orientation, since preferred orientation or rolling texture is developed by heavy cold working, with the result that crystal orientation in the worked metal is itself to some extent dependent on the direction of applied stresses. The distinction between slip and shear may be illustrated by reference to the changes in structure of a face-centred cubic metal after heavy deformation. In such instances the shear direction corresponds to a $\langle 110 \rangle$ direction, the normal slip direction, in all crystals of the predominant rolling texture, i.e. (110) [112], as well as those of the secondary texture (112) [111]. The plane of the shear, however, does not correspond to the normal {111} slip plane, but is near a {112} plane of the primary texture and a {100} plane of the secondary texture. The rolling texture of brass is composed almost entirely of the primary (110) [112] for which there are two possible

$\langle 110 \rangle$ shear directions in each crystal, and these are actually observed. In the rolling texture of copper and cupro-nickel, on the other hand, there is a high proportion of the secondary (112) [111] with only one possible $\langle 110 \rangle$ direction in each crystal, which may account for the fact that in individual crystals of these materials only one family of shear planes is visible.

Further evidence for a change in the deformation process from the normal slip in initial stages to the shear type in later stages is provided by work-hardening curves of many metals in which hardness is plotted against true strain. As the present authors¹⁰ have shown, the change from the initial rapid rate of work-hardening to a subsequent slower rate corresponds in 70 : 30 brass with the change in character of the deformation bands visible in the microstructure of the alloy. The presence of deformation layers situated transversely to the rolling direction also accounts for the difference between transverse and longitudinal strength in heavily rolled metal strip.

III.—STRUCTURAL CHANGES.

The fact that heavy cold working produces changes in the crystalline structure of a metal has been already briefly referred to. These changes in structure consist essentially of the development of a characteristic texture or preferred orientation of the crystal lattice, and fragmentation and distortion of the crystals.

1. *Textures.*

The type of texture or preferred orientation developed by extensive cold deformation of a polycrystalline metal depends both on the crystal structure of the metal and on the mode of deformation. It is convenient, therefore, to classify deformation textures under headings corresponding to the three main types of crystal structure and in each group to deal with the textures produced by tension, compression, and by a combination of the two. Wire drawing is primarily a process involving tension, though frictional effects between wire and die introduce slight modifications to the texture at the surface of the wire, while rolling involves both compression normal to the rolling plane and tension parallel to the rolling direction.

(a) *Face-Centred Cubic Metals.*

(i) *Tension (Wire Drawing).*—As was pointed out in discussing slip, face-centred cubic metals, such as copper and aluminium, possess four families of slip planes, the {111}, and in single crystals slip occurs on the most favourably disposed plane in the most favourably disposed direction. In tension the lattice rotates so that eventually another slip

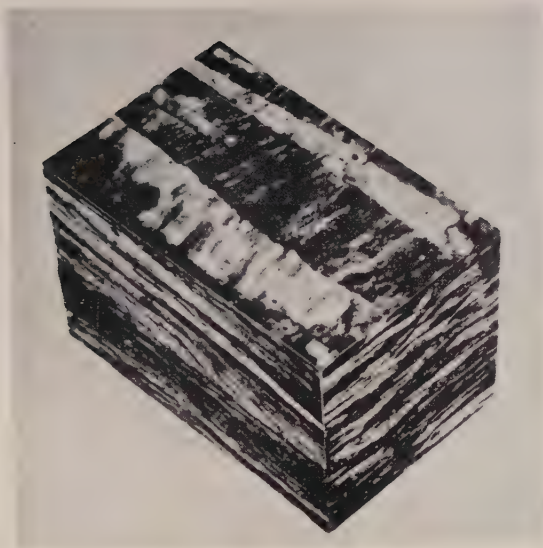


FIG. 1.



FIG. 2.

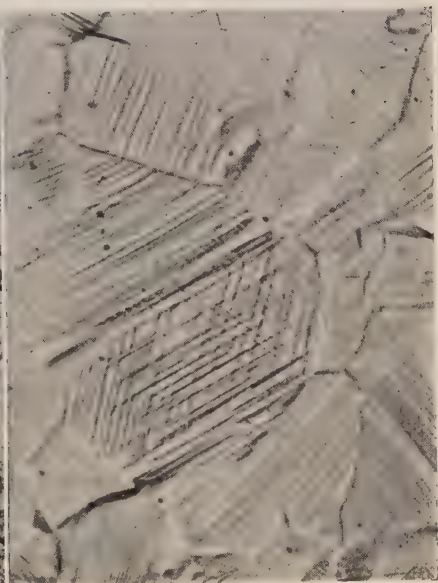
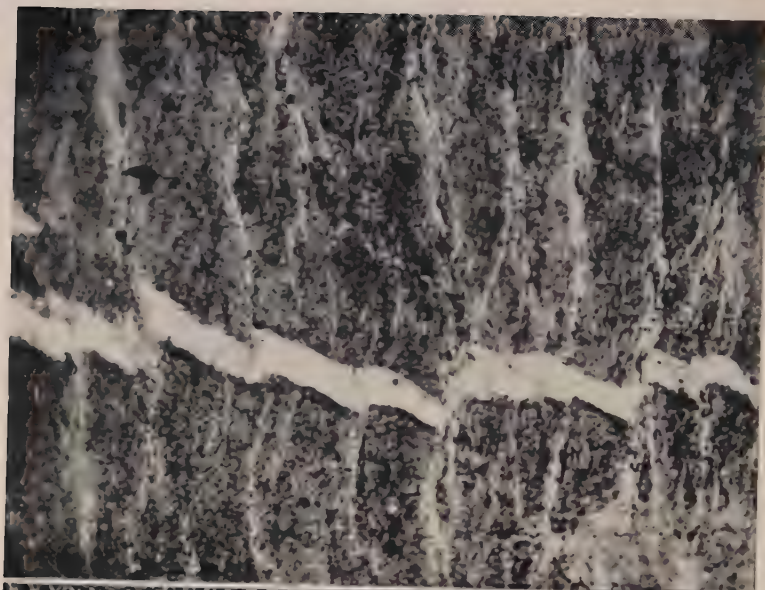


FIG. 3.

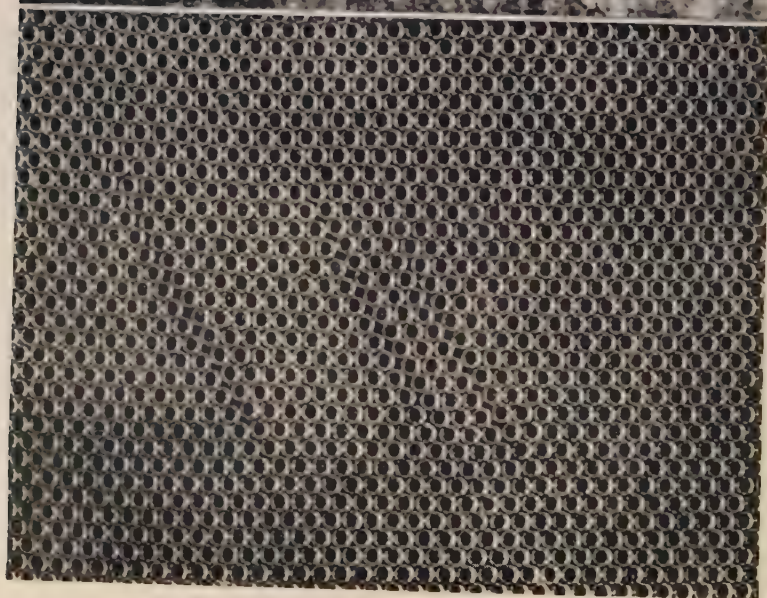
FIG. 1.—A Composite Block illustrating homogeneous deformation in copper strip cold rolled 80%, as revealed by surface, longitudinal, and transverse sections.

FIG. 2.—Surface Appearance of Very Coarse-Grained Zinc after a rolling reduction of about 10%, illustrating fracture of crystals unfavourably oriented for slip. Rolling direction vertical. $\times 3$.

FIG. 3.—Microstructure of Surface of 70 : 30 Brass Strip, showing traces of three families of slip planes produced by 5% extension of an electropolished sample. $\times 400$.



4



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(Fig. 5 by courtesy of the Royal Society.

FIG. 4.—Section Parallel to Surface of Copper Strip cold rolled 80%, showing traces of transverse shear planes coincident with steps in a longitudinal twin band (white). Rolling direction horizontal. $\times 1100$.

FIG. 5.—Parallel Dislocations or structural imperfections in an otherwise regular two-dimensional bubble model. (Bragg and Nye.)

system becomes suitably placed, whereupon slip may proceed by either or both systems. Ultimately a position is reached when the two systems are symmetrical with respect to the applied stress and one of the $\langle 112 \rangle$ axes of the crystal lattice is parallel to the tension axis.

When polycrystalline specimens are deformed by tension or wire drawing, the preferred orientation or texture ultimately developed is also one in which the slip systems are symmetrical about the tension axis. Two such textures have been observed, one with a $\langle 111 \rangle$ axis of the crystal lattice parallel to the tension or wire axis, and the other with a $\langle 100 \rangle$ axis parallel, the crystals of both textures being randomly oriented about the wire axis.

After moderate deformation by drawing, that is, reduction in cross-sectional area of the order of 80%, both textures exist together in most drawn face-centred cubic metals, in proportions which vary from one metal to another. Thus although the $[100]$ texture is predominant in silver, it comprises only about one-fifth of the structure in copper after a 90% reduction, and in this metal the amount decreases as the degree of deformation increases, until after about 99% reduction in area the texture is wholly $[111]$. This is, in fact, according to expectation, since the latter texture has the densest atomic packing in the transverse section of the drawn wire.

A further point of interest is that since, in face-centred cubic metals, the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions are those in which Young's modulus of the material is at a maximum and minimum, respectively, cold drawing always leads to an increase in modulus along the wire axis when the $[111]$ texture is predominant, an effect which is particularly noticeable in a metal with a high degree of elastic anisotropy such as copper.

The textures just described occur in the central zone of cold-drawn wire. Near the surface a modified texture is observed resulting from inhomogeneity of plastic flow due to friction between the surface and the die. In copper, for instance, at the surface, texture is not well developed though, as at the centre, it has a $\langle 111 \rangle$ axis parallel to the wire axis. In the zone intermediate between surface and centre the texture axis is inclined at about 10° to the wire axis, the inclination decreasing as the centre of the wire is approached.

(ii) *Compression*.—The texture of polycrystalline specimens of face-centred cubic metals resulting from deformation in compression is similar to that of the single crystal, in that a $\langle 110 \rangle$ axis of the crystal lattice lies parallel to the compression axis. Secondary textures, however, are present in polycrystalline materials, the most common being a $[100]$ texture, but in 70 : 30 brass a subsidiary $[111]$ texture has been observed.

(iii) *Tension and Compression (Rolling)*.—After deformation by cold rolling the individual crystals lie with either a $\{110\}$ plane parallel to the strip surface and a $\langle 112 \rangle$ direction in that of rolling, or with a $\{112\}$ plane and $\langle 111 \rangle$ direction so placed. These two arrangements are usually referred to as the (110) [112] and (112) [111] rolling textures. In strip of pure metals such as copper and aluminium both textures occur together, the (110) [112] predominating, but with increasing amounts of alloying elements the secondary (112) [111] texture becomes less marked.¹¹

(b) *Body-Centred Cubic Metals.*

(i) *Tension (Wire Drawing)*.—In discussing slip mechanism it was mentioned that, in all the body-centred cubic metals which have been studied, slip occurs in the close-packed $\langle 111 \rangle$ direction, but that the slip plane may be $\{112\}$, $\{110\}$, $\{123\}$, or, as in α iron, all three together. Since deformation texture is a function of the active slip planes, it cannot be assumed that the textures developed in all body-centred cubic metals are the same, but in drawn iron, tungsten, and molybdenum wires a common [110] fibre texture occurs.

(ii) *Compression*.—There is as yet little information on compression textures of body-centred cubic metals, but it has been established that in α iron and α iron-silicon alloys a [111] fibre texture is predominant, accompanied by small amounts of [100].

(iii) *Tension and Compression (Rolling)*.—Study of rolling textures in body-centred cubic metals has been confined to iron and its alloys and here preferred orientation is developed after rolling reductions varying from 30 to 60%, becoming more marked as the degree of reduction increases, though owing to the complex nature of slip in these materials the textures developed cannot be described as a combination of those produced by simple tension and compression. In low-carbon steels the texture produced by reductions of 95–98.5% consists of crystal orientations in which the $\langle 110 \rangle$ directions are approximately parallel to the rolling direction and the $\{001\}$ planes parallel to the strip surface, although deviations from the latter conditions up to 50° each way about the rolling direction may occur. The texture of heavily rolled α iron-silicon alloys is similar to that just described, namely (001) [110], and the control of textures in these alloys is of considerable importance in the manufacture of transformer laminations, in order to take advantage of the high permeability in the $\langle 100 \rangle$ direction.

(c) *Close-Packed Hexagonal Metals.*

(i) *Tension (Wire Drawing)*.—When single crystals of close-packed hexagonal metals such as magnesium and zinc which possess only one

family of slip planes, the (0001) or basal planes, are deformed in tension, the orientation of the crystal lattice changes so that the slip plane and the operative slip direction both lie more nearly parallel to the axis of tension. But as the slip plane approaches the tension axis it is less favourably oriented for slip since the resolved shear in the plane decreases, so that further deformation occurs by twinning on {1012} planes.

In polycrystalline specimens moderate deformation by tension gives rise to preferred orientation or texture in which the (0001) or slip planes of the individual crystals are aligned parallel to the applied tension or wire axis, but are randomly oriented around it. More severe deformation causes twinning, so that in the final texture the (0001) planes are displaced, and in zinc, for example, they lie at an angle of 20° to the wire axis.

(ii) *Compression*.—Compression of hexagonal metals causes deformation by slip accompanied by rotation of the crystal lattice, so that the basal (0001) plane is eventually normal to the axis of compression.

(iii) *Tension and Compression (Rolling)*.—Since rolling involves both compression normal to the rolling plane and tension parallel to the rolling direction, it would be expected that the texture of rolled hexagonal metals would be such that the single family of (0001) basal planes lies nearly parallel to the strip surface. This type of texture is actually observed in magnesium, which has an axial ratio of 1.624 approximating to that of a system of close-packed spheres, viz. 1.633.

In zinc and cadmium, however, whose axial ratios are greater, 1.865 and 1.885, respectively, the hexagonal axis is displaced in the rolling direction at an angle of about 20° to the normal. In rolled beryllium, zirconium, and titanium, however, which have axial ratios of 1.568, 1.592, and 1.587, respectively, smaller than that of close-packed spheres, there is also a displacement of the hexagonal axes of individual crystals about the normal to the strip surface, but in the transverse direction. Such modifications of the expected texture are probably caused by twinning or kinking.

(d) *Recrystallization Textures.*

Textures developed by cold working are of practical importance not only in determining the properties of metals in the worked condition, but also because they can exert a profound influence on the structure which results on subsequent annealing. When heavily cold-worked metals recrystallize, the preferred orientation either remains substantially the same, as in wires, or transforms, as in metal strip, to a completely different but related orientation^{9, 10} or characteristic recrystallization

texture. Since preferred orientation gives rise to anisotropy in metal strip,¹² a full appreciation of the factors responsible for the development of textures is essential in the production of strip suitable for deep drawing.

2. *Fine Structure.*

The fact that single metal crystals begin to deform by slip at very much lower shear-stress values than would be expected from theoretical considerations led early investigators to suppose that there are defects in the structure, such as the micro-cracks and lattice misfits postulated by Griffith¹³ and Smekal,¹⁴ which function as local stress-raisers. Later Orowan,¹⁵ Polanyi,¹⁶ and Taylor¹⁷ suggested that the existence of crystal-lattice defects on an atomic scale, termed dislocations, would account for the relatively low strength of metals and their capacity for work-hardening. The concept of dislocations has since been developed considerably to explain further effects such as characteristic yield and strain-ageing, and a comprehensive survey of the dislocation theory has recently been made by Cottrell.¹⁸

Lattice imperfections probably exist in the most regular array of atoms, such as single crystals, and most certainly at discontinuities in structure such as crystallite boundaries. It should be realized, however, that since dislocations are on an atomic scale there is at present no direct experimental evidence for their existence, and the various types of dislocation which have been discussed simply represent possible forms of imperfections that might be expected to occur in otherwise regular atomic arrays. A simple instance of dislocation has been demonstrated by Bragg and Nye¹⁹ in a two-dimensional raft of bubbles, in which glide takes place between two parts of the raft by the progression of a dislocation or bubble misfit along a line of close-packed bubbles as depicted in Fig. 5 (Plate LII) reproduced from their paper.

Assuming that dislocations are present at crystallite or crystal mosaic boundaries, the low yield strength of metal crystals can be explained on the basis that slip takes place by the movement of dislocations without appreciable increase in the energy of the crystal as a whole. On application of a stress greater than that just necessary to cause movement, the dislocations are accelerated to high energies and further dislocations thus generated. Each dislocation is a centre of local lattice distortion, and is therefore surrounded by a stress field, so that, when the density of dislocations becomes high, their motion is retarded by the mutual interaction of these fields, and thus the progressive increase in resistance to deformation by cold work, that is, work-hardening, is explained.

Deformation by motion and generation of dislocations must, of necessity, be associated with a high degree of lattice strain, lattice bending, and crystallite formation, and detailed investigations are being made of these aspects of fine structure in cold-worked metals. Although, as pointed out above, there is as yet no direct evidence for the existence of dislocations, nevertheless this work has provided a considerable amount of information about the fine structure of deformed metals, all of which is entirely consistent with the assumption of dislocations. Most of this has been concerned with the interpretation of anomalies in the X-ray-diffraction patterns of highly deformed metal specimens, namely, asterism in Laue patterns, broadening of Debye-Scherrer lines, and finally decrease in line intensity and heightening of background intensity, all of which become more marked as the extent of deformation is increased. Broadly speaking, the weight of experimental evidence indicates that these effects are due to the break-up of the primary crystals into smaller crystallites, the lattice of which is in a state of strain.

Wood and Rachinger²⁰ have established that in homogeneously deformed polycrystalline specimens, the degree of line broadening is dependent on crystallite size only, and by this means have estimated that the crystallites in deformed specimens of several metals range in size from 2.4 to 4.2×10^{-6} cm. Quantitative estimates of lattice strain are best derived from measurements of the decrease in line intensity²¹ of Debye-Scherrer patterns which accompanies increase in plastic deformation of the specimen. This decrease in intensity is similar to that observed on raising the temperature of the specimen, and the atomic displacements in the strained lattice are, therefore, regarded as equivalent to those due to thermal agitation, except that the former are fixed. On this basis, mean atomic displacements can be calculated and the total strain expressed as energy stored in the distorted metal. While energy content calculated in this way by Boas²² is of the same order of magnitude as that determined by direct measurement,²³ the former is usually several times greater than the latter, e.g. for copper 7.4 and 1.15 cal./g., respectively, and Boas has suggested that this is probably due to the fact that groups of atoms, rather than single atoms, are displaced in the strained lattice.

Further information regarding fine structure in deformed metals is provided by a study of the asterism effects in Laue patterns from cold-worked single crystals.²⁴ Asterism is probably due to bending or distortion of the crystal lattice, since, for example, the effect is observed in zinc specimens after bending, but not after deformation by simple shear. If the specimen is then annealed the asterism streaks in the

diffraction pattern become striated, indicating that the strain has been relieved by the break-up of the primary crystal into a number of crystallites with slightly differing orientation. This phenomenon, which is referred to as polygonization, is probably identical with the process of lattice recovery in the present authors' kinetic theory of recrystallization²⁵ and the recrystallization *in situ* described by Crussard.²⁶ This striated asterism occurs spontaneously in the pattern of single crystals of sodium and potassium deformed at room temperature, and also of single crystals of lead deformed by creep, and this supports the view that the crystallites in plastically deformed metal are, in fact, formed by polygonization or lattice recovery.

Accepting the view that in cold-worked metal the original crystals have been broken up into elastically strained crystallites, Bragg²⁷ has put forward an explanation of the yield of metals, based on the assumption that yield is associated with relief of elastic strain in crystallites by internal displacement over one interatomic distance. This hypothesis has been further developed by Wood and Rachinger,²⁰ who, using a refined experimental technique for deriving crystallite size from line-broadening effects, have calculated values for the ultimate tensile strength of cold-worked metals which agree well with those determined by direct measurement.

IV.—RELATIONSHIP BETWEEN STRUCTURE AND WORKABILITY.

1. *Work-Hardening.*

One of the most characteristic properties of metals, and one which is of the greatest practical importance, is their capacity for work-hardening, which, as already explained, is attributed to interaction between stress fields surrounding dislocations, the number of which increases progressively with deformation. Stress has a directional character and hence when, during plastic deformation, dislocations associated with stresses in opposed directions meet, the stress fields cancel each other and the dislocations disappear. As deformation continues, therefore, the increase in the number of dislocations is accompanied by an increase in the number of those being cancelled, and a state of equilibrium is reached when the number of dislocations disappearing is equal to the number being formed. This explains the fact that there is a limit to the degree to which a metal can be work-hardened.

Furthermore, it is to be expected that the limit to the number of dislocations, and consequently to work-hardening, will be reduced by a rise in temperature and increased by greater rates of strain. While such effects are of little significance in the limited range of temperatures and rates of strain employed in industrial cold-working operations, their

existence has nevertheless been demonstrated in experiments^{28, 29} carried out under a wider range of conditions.

The assumption that the limiting density of dislocations decreases with increase in temperature of deformation, may be expressed in another way by saying that the nearer a metal is to its melting point the smaller the number of dislocations present after deformation, and hence the lower its resistance to deformation. It is therefore clear that the work-hardening capacity at room temperature of pure metals, say, for instance, lead, aluminium, and copper, will be in the same order as their melting points.

The dislocation theory also accounts for the effect of foreign atoms in increasing the resistance to deformation and the work-hardening capacity of a metal, whether present in small quantities as impurities or deliberately added, as in the industrially important solid-solution alloys. According to Cottrell¹⁸ there is an attraction between dislocations and foreign atoms in a crystal lattice, so that the latter migrate to and are concentrated about dislocations. The latter can then move only under greater applied forces or, in other words, hardness and resistance to deformation are increased. Furthermore, the reduction in mobility of the dislocations arising from their solute atmospheres means that the limiting dislocation density during plastic deformation is raised, leading to greater capacity for work-hardening.

The stabilizing of dislocations is, however, not the only effect of solute atoms, since the presence of atoms of different sizes, whether concentrated around dislocations or not, introduces lattice strains, evident from changes observed in lattice parameter, and these strains interfere with the slip mechanism. Furthermore, Dorn and his collaborators³⁰ consider that solution-hardening depends not only on lattice strain but also on changes in electron concentration brought about when one metal dissolves another of different valency. Thus, silver dissolved in aluminium produces no change in lattice parameter, since the atoms are of similar sizes, but nevertheless increases its resistance to deformation. Support for this view is provided by the fact that binary alloys made by dissolving different solutes in the same solvent have the same stress/strain relationships in tension, providing the solutes are present in equivalent amounts, equivalence being assessed from lattice-parameter and electron-concentration changes. That there is, in fact, a linear relation between hardening by solution and work-hardening capacity has been indicated by Brick *et al.*,¹¹ an element which confers great solution-hardening, producing a correspondingly great increase in work-hardenability.

Migration of solute atoms to dislocations accounts also for the

sudden yield characteristic of low-carbon steels, for strain-ageing, and for the acceleration of age-hardening by cold working. Sudden yield is observed when migration is rapid, a condition which prevails in carbon steels under stress at room temperature, while strain-ageing occurs in alloys where migration is more sluggish, so that equilibrium is not reached during the actual deformation process. Migration rate increases rapidly with temperature, so that strain-ageing is also accelerated by a rise in temperature, which explains the initial increase in hardness with increase in annealing temperature frequently observed in the annealing curves of cold-worked alloys. The acceleration of age-hardening by cold working is related to the increase in the number of dislocations during plastic deformation which provides the nuclei for the local concentrations of solute atoms responsible for age-hardening.

2. *Ductility.*

Another characteristic and important property of most metals is ductility. This term is often used to signify the extent to which a metal can be cold worked by various processes, but in what follows it is used in the restricted sense of capacity for uniform elongation under tension. Ductility as thus defined is directly related to work-hardening, since a tensile specimen elongates uniformly until the increase in strain-hardening is insufficient to balance the increase in stress consequent on the reduction in cross-sectional area of the specimen. It is for this reason that a metal like lead, which exhibits little, if any, work-hardening at room temperature, is much less ductile than copper, for example, which has considerable work-hardening capacity.

In copper and copper alloys, at least, the extent of uniform elongation corresponds to the amount of deformation which can occur by slip alone, e.g. the limit of uniform elongation of 70 : 30 brass is about 65%,³¹ equivalent to a rolling reduction of 40% in thickness, and this latter corresponds to the stage in rolling where the mode of deformation changes from slip to shear as indicated by the appearance of shear bands in the microstructure.¹⁰ In short, the metal elongates uniformly under tension only so long as deformation occurs by slip. This explains why a cold-worked metal is less ductile than it is in the unworked state, since a proportion, or all, of the slip deformation has already taken place. Sachs and his co-workers³² have, in fact, established that there is a direct relationship between amount of prestraining and remaining ductility. In investigating the ductility of an age-hardened aluminium alloy they found that if the amount of prestraining effected by simple tension, wire drawing, or rolling, was less than that equivalent to uniform elongation, then the total ductility, that is, the sum of elongation equivalent to the prestrain plus retained or residual ductility

as measured in a tensile test, had a constant value, being equal to the uniform elongation of the material in the undeformed condition. When the degree of cold-working prestrain is equal to, or exceeds, the slip deformation, then the retained ductility is practically zero.

Although uniform elongation in simple tension is a useful guide to the suitability of metal strip for drawing or pressing operations, it does not necessarily represent the total amount of deformation that can be effected in these operations under conditions other than that of simple tension. In fact, total strains considerably in excess of those equivalent to the limit of uniform elongation by simple tension are effected in practice as, for instance, in wire drawing, when the reduction per pass is adjusted so that the load required to pull the wire through the drawing die at any given stage never exceeds the breaking load of the drawn wire.

3. Plasticity in Compression and Rolling.

The true stress/strain relationship in the homogeneous deformation of a metal is the same both in compression and tension.⁶ Since, however, the cross-sectional area of material under compression increases progressively, there is, in compression, no departure from homogeneous deformation comparable with the necking which occurs in tension, nor, therefore, a limiting value of plasticity corresponding to the limit of uniform elongation under tension. While the latter can be measured directly in the course of a tensile test, the determination of resistance to homogeneous deformation in compression can be made only by indirect methods³³ because of the complications arising from friction between the metal and the constraining tools. Friction is, indeed, a highly significant factor in determining, and hence controlling, the magnitude of the actual loads required in such industrial cold-working operations as rolling.³⁴

While many metals can be deformed in compression almost indefinitely, the beating of gold leaf is, perhaps, one of the few examples in which cold working is continued to an extreme stage, although some other metals are produced as thin foils by rolling without annealing. The extent, however, to which metals and alloys are reduced in industrial cold-working processes is determined more often by such factors as the capacity of available plant, economic aspects of power requirements for working metal in the hard condition relative to the cost of intermediate annealing operations, and by metallurgical considerations such as the need to control the texture of the final product. Certain industrial operations depend for their success on a sufficiently high rate of working being maintained to raise the temperature and thereby render possible additional modes of deformation or cause partial softening, as, for example, in the cold rolling of zinc and in the impact extrusion of several metals and alloys.

4. *Cold Working of Polyphase Alloys.*

In alloys consisting of more than one phase, deformation of the separate constituents conforms, as far as is known, to the crystallographic mechanisms established for pure metals and single-phase alloys, but the cold-working capacity of the alloy as a whole may be appreciably affected by the form and distribution of the various phases. The simplest case is where a relatively small proportion of a second phase exists in the form of discrete particles, or islands, in the continuous phase or matrix, and the effect of these particles on the workability of the alloy depends upon their shape, size, and distribution, as well as upon the work-hardening properties of both phases. An included phase may, of course, be harder or softer than the surrounding material and may be plastic or brittle, but it is of importance to note that, in some circumstances, a substance which is inherently brittle may exhibit considerable plasticity when confined in a ductile phase. For instance, Schnell and Scheil³⁵ have established that sulphide inclusions in a steel fracture and break up when near to the surface of the metal, but are deformed plastically when located in the interior and therefore subjected to pressure from all sides.

In a duplex system, there is a tendency for the softer of two phases to deform more than the harder. The relative deformation is not wholly dependent, however, on the separate work-hardening characteristics of the constituents, but is governed by the general principle of minimum work. A hard included phase is deformed less than the surrounding metal only as long as the work required to effect this, and to flow the matrix around it, is less than that required to deform the matrix itself. Conversely, a soft included phase is deformed more than the major phase only until the work involved becomes equal to that required for homogeneous deformation. Thus, in both types of alloy the deformation tends to become homogeneous with heavier cold-rolling reductions. Tin bronze and leaded brass provide good examples of these effects, and Unckel³⁶ has shown that the deformation of the hard δ phase in ($\alpha + \delta$) copper-tin alloys when cold rolled is, at all reductions, less than that of the whole specimen or of the matrix, but its reduction relative to that of the α phase increases with increasing rolling reduction. Lead in α brass, on the other hand, deforms during rolling more than the surrounding α phase in the earlier stages, but after about 50% rolling reduction the matrix deforms equally with the lead.

Many industrially useful alloys contain, generally in small proportions, phases so hard and brittle that they do not deform plastically irrespective of the extent and manner of the deformation to which the alloy is subjected. For example, commercially pure aluminium and

several aluminium alloys contain, when cast, inclusions of complex aluminium-iron-silicon phases either as lamellæ, which are extremely detrimental in both hot and cold working, or as more compact, equiaxed particles which are much less harmful. Furthermore, after heavy rolling reductions lamellar phases break up to a greater degree than equiaxed constituents, resulting in increased formation of stringers of small particles which, in turn, give rise to a mechanical, as distinct from crystallographic, directionality. The form of the constituent phases can, however, be favourably changed by slight compositional adjustments. For example, an increase in the ratio of iron to silicon tends to diminish the proportion of the lamellar form of the aluminium-silicon-iron compound, while small manganese additions effect a still greater improvement by changing the types of compound present and their dispersion in the matrix.

A change in form and distribution of a hard brittle phase may have even more striking effects on the workability of a metal. Thus Merica and Waltenberg³⁷ showed that in pure nickel as little as 0.005% of sulphur, present as low-melting-point Ni_3S_2 , was distributed around grain boundaries and rendered the metal unworkable either hot or cold. Alloying with a small amount of manganese or magnesium, however, resulted in the formation of high-melting-point sulphides in the form of small uniformly distributed particles, and workability was completely restored.

Age-hardening alloys fall in the heterogeneous category from the point of view of cold working, since, during at least some of the fabrication processes, they consist of more than one phase. It is the mode of occurrence of the second phase, present in only minor proportions, and the degree to which its separation has progressed, which largely determine resistance to deformation. Thus after solution heat-treatment resistance to deformation rises to a maximum as age-hardening progresses, and then decreases on over-ageing.

The first part of the pronounced increase in hardness during an ageing treatment is attributed to interference with the slip mechanism by lattice distortions arising from local concentrations of solute atoms, the first stage of precipitation. Once particles of precipitate, having a crystal structure different from that of the matrix, have been formed, hardening continues to increase as long as the lattices of the matrix and precipitate can accommodate each other by mutual strain, a condition termed coherency. During this stage the hardening corresponds to an increase in the magnitude of the strains surrounding the precipitate. Softening due to over-ageing, on the other hand, results from relief of these strains, and a number of contributing factors, for instance, loss of coherency as the precipitate particles increase in size and subsequently solute depletion of the matrix, have been suggested. The phenomenon

of age-hardening demonstrates, therefore, that the resistance to deformation of heterogeneous alloys is highly dependent on the strains to which the matrix crystal lattice is subjected by the mode of occurrence of subsidiary phases.

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LUBRICANTS FOR THE COLD WORKING OF **1287** NON-FERROUS METALS.*

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SYNOPSIS.

The processes of cold rolling, press drawing, tube drawing, and wire drawing are discussed from the point of view of the demands they make on lubricants. Suitable types of lubricant are suggested in each case.

THE part played by lubricants in the cold working of non-ferrous metals is of paramount importance. Indeed, the lubricant selected for any particular cold-working operation is the factor that determines, as much as any other, whether the metal-forming operation is a failure or a success.

Although non-ferrous metals have been cold worked for many years, it is found, even at the present time, that despite the wealth of practical experience obtained, no greater lack of uniformity exists in any of the varied processes employed than in the selection and application of the forming lubricants. Although this would appear to be a condemnation of both the cold metal-working and the petroleum industries, it must be appreciated that this subject, particularly cold rolling, is one in which the practical experience of the operative has far outstripped the fundamental knowledge of the theorist. Because of this lack of fundamental knowledge, the selection of the most appropriate lubricant for any particular operation is usually made on the basis of trial and error, with the skill of the individual operative playing an important part. It is with an appreciation of this fact, and in an endeavour to obtain some uniformity of thought and achievement, that an attempt is made here to assess the lubrication requirements of some of the non-ferrous cold-working operations, and to interpret them in the light of practical experience.

I.—COLD ROLLING.

1. *Fundamental Aspects of Rolling.*

While it is true that certain operations, such as skin or temper passing, are carried out primarily to effect improvements in surface finish and physical characteristics of the metal, the main function of

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cold rolling is to reduce the cross-sectional area of a given piece of metal by the greatest amount during any one pass. Although there are several theories regarding the actual physical changes which occur during reduction, it is intended here to consider the two principal view points only.

As the cross-sectional area of the strip is being reduced while the volume of metal entering and leaving the rolls remains constant, the speed of the metal leaving must obviously be greater than that entering. The main difference in the theories centres around the point whether this increase in speed is accompanied by slippage between the rolls and the strip surfaces. The generally accepted view is that the strip surface is moving more slowly than the rolls at the point of contact on the entry side. The speed of the strip gradually increases to a point where it attains a speed equal to that of the rolls at the neutral or "no slip" point; thereafter, the speed continues to increase and the metal leaves the rolls on the exit side moving at a higher speed than the rolls. This theory is supported by the fact that it can be shown that reduction in the coefficient of friction, by the use of suitable lubricants, also reduces the work load on the mill.

Others hold that no appreciable slippage takes place and that the increased speed of the strip at the exit side of the rolls is due to the plastic flow of the metal, the action being similar in nature to extrusion. If this theory were true, the roll lubricants would be expected to function as coolants in dissipating the heat of internal friction. The fact that zinc, which has an extremely high internal resistance to plastic flow, is a particularly difficult metal to roll, owing possibly to the large amount of heat generated during reduction, may lend some support to this belief.

It is considered that the theory of slippage between the strip and the rolls permits an explanation of some of the performance data obtained in practice. These data indicate that the coefficient of friction and the film strength are two of the most important characteristics of roll lubricants. These properties accord more closely with the assumption of metal surfaces moving with respect to one another than with the conception of internal plastic flow. It is quite possible that the ultimate reconciling of these two view points will result in the discovery that both play a significant part, but that the former is of the greater significance as regards the lubricant employed.

If the fact that slippage between the strip and the roll occurs, be accepted, it must be apparent that under certain conditions it would be possible to increase the lubricity of the roll lubricant, and thereby reduce the friction between the strip and the roll, to such an extent

that it would be impossible to roll at all. The selection of the appropriate roll lubricant must not, therefore, aim at the elimination of friction, but at keeping it under proper control.

2. Desirable Characteristics of Roll Lubricants.

(a) Film Strength.

Where reductions per pass are heavy and mill speeds are high, it is essential that the roll lubricant should have adequate film-strength characteristics to prevent metal-to-metal contact under the boundary conditions of lubrication that exist between the strip and the roll. If the film-strength properties are inadequate, the desired reductions cannot be made without excessive power consumption and breakage of the strip. Because of the extremely high unit pressures between the rolls and the strip at the roll nip, the selection of the rolling oil base stock assumes importance. The viscosity of all oils increases with pressure, but the pressure/viscosity ratio is not constant for all types. This subject is being investigated in the extremely high-pressure range, and, although the work has not been completed, it is already known that the pressure/viscosity ratio is a function of the viscosity index of the oil: the higher the viscosity index of the base oil, the less is its viscosity affected by pressure. Because of this, oils of low viscosity index have certain advantages as rolling lubricants, in so far that for the same initial viscosity at atmospheric pressure, they are much more viscous than oils of high viscosity index under the conditions of high pressure which exist at the roll nip, where additional film strength is required.

Moreover, certain additives can impart film-strength properties to a lubricant that will promote slippage of the rolls on the strip, but what are commonly referred to as extreme-pressure ingredients are not suitable in this application because of their surface activity.

(b) Viscosity.

If the viscosity of the roll lubricant is too high, slippage of the work rolls on the strip may occur, and unsatisfactory strip will be produced. In addition, the higher the viscosity of the oil, the higher will be the temperature at which it can be completely removed from the strip—a factor of importance in producing clean annealed strip. It is necessary, therefore, in some rolling applications to maintain the viscosities of the finished rolling oils within rather critical limits. In some types of rolling mills where the rolling oil has also to function as the mill lubricant, an additional complication arises, for in such an installation it is extremely unlikely that the most appropriate rolling oil is also the most

satisfactory lubricant for the mill, and in such a case the selected product must be a compromise between the requirements of each.

(c) *Ease of Removal.*

Where it is necessary to remove the roll lubricant from the strip before annealing, it is important that residual films on the strip should be readily removable. Any stains that develop during annealing operations are objectionable in most cases, and intolerable where the strip has subsequently to be coated.

While it would be very desirable to have a rolling oil which would flash off at a conveniently low temperature, petroleum oils unfortunately have a boiling range as opposed to a fixed boiling point. Despite this, however, petroleum rolling oils are produced which have a sufficiently narrow boiling range to permit clean annealing to be achieved. The following boiling range is typical of an oil which has proved to be satisfactory for both copper and aluminium finish rolling :

	°C.
Initial Boiling Point . . .	278
10%	292
30%	298
40%	306
50%	310
60%	313
70%	317
80%	321
90%	330
95%	342
Final Boiling Point . . .	350

(d) *Freedom from Staining.*

In most rolling applications, the rolling lubricant is not removed from the metal before annealing, and in such instances, the rolling lubricant should be essentially non-staining in character.

(e) *Rolling Properties.*

Broadly speaking, the higher the oil viscosity (within practical limits) the greater will be the reductions obtained per unit roll load. On the other hand, high-viscosity oils do not produce such good surface finish and may contribute to dirty annealing. Light-viscosity oils normally produce good surface finish and give cleaner annealing, though the reductions per unit roll load are not so great as with high-viscosity oils. On the above broad basis, and in order to benefit from the virtues of the lighter-type oils, the aim is to build load-carrying and lubricity characteristics into them by using suitable additives. By so doing, it is possible to utilize to a considerable degree, the benefits from both light and heavy oils, and eliminate their respective deficiencies,

The extent to which viscosity and appropriate additives are adjusted in rolling oils cannot be determined from a rigid formula. This can be readily appreciated from the fact that a great many variables are involved, and it is virtually impossible to have an exactly similar set of conditions on any two mills. Because of this, the formulation of the most suitable rolling oil for any particular material and rolling programme must be adjusted to meet a fixed set of conditions. It has been found in many cases that an alteration to one variable in a rolling programme makes necessary the adjustment of others in order to produce the desired results; and very often this adjustment has to be made in the rolling oil.

(f) *Chemical Stability.*

With the increasing use of recirculation rolling-oil systems containing large volumes of oil, an additional characteristic, which has not been necessary hitherto, is now required. Where an oil is recirculated and subjected to high temperature, chemical stability or resistance to oxidation assumes great importance. This can be appreciated when the cost of recharging a system containing many thousands of gallons of rolling oil is considered.

3. *Rolling of Copper and Copper Alloys.*

The cold rolling of copper and copper alloys can be carried out on either reversing or non-reversing two-high or four-high mills. Rolling speeds are relatively low compared with those for some other metals, and although some units are known to operate at 600 ft./min., normally speeds are considerably slower.

Because rolling speeds are relatively low, cooling does not present a major problem. The application of rolling oil is therefore on an "all loss" basis—usually by drip or spray to the rolls and strip. In addition, however, application is made by passing the strip through a bosh containing water with a thin film of rolling oil on the surface. It is claimed that this method of application permits even distribution of the rolling oil on the strip much more economically than is achieved by drip or spray application. Experiments have been made with flood application and recirculation of the rolling oil, but in systems of this type adequate means of removing fines and other extraneous material are necessary. It has been accepted at this stage, with the existing low rolling speeds, that flood application of the rolling lubricant is not necessary.

The use of soluble oil emulsions as rolling lubricants has been

investigated on a production basis with some measure of success, but the soluble oils should preferably be of the special non-ionogenic type and should not be confused with normal soluble oil in general use for machining operations. They must be as nearly neutral as possible. Too high a percentage of free fatty acid can react unfavourably on copper and copper alloys. Where special soluble oil emulsions are used in this application, it is essential that they should be kept in a clean condition. Unless adequate facilities for settling, skimming, and filtration are provided, the recirculation of fines to the strip may cause undesirable stains. For strip which requires a high finish and a clean surface, this condition cannot be tolerated.

Conventional-type soluble oils are unsatisfactory for copper rolling because they tend to produce staining during annealing, owing to the presence of alkaline ash-forming ingredients. Technological research is opening the door to the production of soluble oils made from mineral oils and suitable emulsifiers. Such soluble oils are reasonably stable. For the cold rolling of copper and copper alloys it is generally accepted that, where a high finish is required, non-soluble oils produce the most satisfactory strip.

The selection of appropriate rolling oils given below is suggested after a great many practical tests, but here again, because of the number of variables involved, basic recommendations are not always applicable.

Generally speaking, copper-rolling lubricants are divided into two broad categories: (a) intermediate and (b) finishing oils. In the breaking-down process the surface finish of the strip is not very important, but maximum reductions per pass are required. In order to cater for this condition, a fairly heavy-bodied oil (by rolling-oil standards) is selected. It is suggested that an oil of at least 43 Centistokes at 100° F. (38° C.) should be used, and for maximum reductions it should preferably contain lubricity and film-strength additives. For finish rolling, where a high surface quality is essential, a very much lighter oil should be employed. In order to obtain the maximum reductions together with good finish, suitable lubricity and film-strength additives should be incorporated in an oil of about 4–6 Centistokes at 100° F.

In selecting the base oils for copper rolling, due attention should be paid to their ability to give clean annealing. In this respect they should have a sufficiently narrow boiling range to permit all the oil to come off at the annealing temperature, thereby preventing the formation of stains on the finished strip. In addition, they should have a sufficiently low sulphur content to obviate staining. It is generally believed that, if the sulphur content is below 0.5%, no staining troubles should be encountered.

4. *Rolling of Aluminium and Aluminium Alloys.*

The cold rolling of aluminium and aluminium alloys, like that of copper alloys, can be carried out on either reversing or non-reversing two-high or four-high mills, but the modern trend is to utilize four-high tandem mills for maximum production.

The cold rolling of aluminium to sheet—and particularly to foil gauges—has been regarded by aluminium processors for many years as an art, the methods of rolling and the lubricants being treated as trade secrets. In most aluminium cold-rolling mills, both in this country and the United States, a wide variety of rolling oils have been used. However, within recent years an attempt has been made to achieve some degree of uniformity throughout the industry.

For most cold-rolling operations to sheet gauge, a light mineral oil with a viscosity of about 4–6 Centistokes at 100° F. (38° C.) is used in conjunction with film-strength and lubricity additives. Originally the additives used were of the fatty-oil type, but in recent years these have largely given way to chemical additives, as these usually come off at a temperature much lower than do the fatty oils.

Although the application of rolling oil is frequently on an “all loss” basis, by drip or spray to the rolls and sheet, with the increased rolling speeds now quite common, heat removal has necessitated flood application. Flood application is normally provided by a series of spray pipes to both top and bottom work-rolls and to the strip on the ingoing side of the mill and frequently on the exit side too.

As in the case of copper rolling, it is highly important that the rolling oils should possess clean annealing characteristics.

5. *Filtration of Rolling Oil.*

Because of the small particle size of the aluminium fines with which the rolling oil becomes contaminated, filtration presents a major problem. Despite the fact that the rolling oil itself is capable of giving clean annealing, the build-up of aluminium fines in the oils—particularly when this approaches a figure of between 0.1 and 0.2%—contributes to over-heating as a result of the friction produced between the rolls and the strip, and also to dirty annealing owing to deposition on the strip.

The impurities with which aluminium rolling oil becomes contaminated are almost colloidal and, because of this, it is virtually impossible to remove them with mechanical filters; only absorbent-type filters are capable of dealing with them. Filters of this kind normally utilize fuller's earth or similar materials and, although they are capable of removing all traces of contaminants from the oil, they tend to remove also some of the fatty materials. As chemical additives do not appear

to be affected to the same extent by the absorbent filtering media, oils containing materials of this type are preferred.

In the United States fatty additives are used to a much greater extent than chemical additives, and in order to prevent their removal in earth filters, it is necessary to heat the oil up to at least 110° F. (43° C.) and preferably higher before filtration. This creates an additional complication in so far that two heat-exchangers have to be incorporated in the rolling-oil system—one to raise the oil temperature before filtration and another to cool it before its return to the mill. This factor alone weighs heavily in favour of oils containing chemical additives. The temperature of the rolling oil applied to the mill varies to some degree, but is usually between 75° and 85° F. (24° and 29° C.)

Because of the large volume of oil circulated in high-speed mills, earth filters are never used on a full-flow basis. Normally, by-passing 20% of the total circulated volume is adequate to keep the oil sufficiently clean to produce acceptable strip for sheet rolling; but in the case of foil rolling, where the particle size of the fines is much smaller, this figure may have to be raised to 50–60%.

The preceding is, of course, only a broad guide, as it must be appreciated that the percentage of rolling oil that should be treated in an absorbent-type filter is a function of the total quantity of rolling oil in circulation.

Absorbent-type filtering material has a limited life, and because this necessitates recharging of the filtering equipment at regular and fairly frequent intervals, it should not be called upon to deal with impurities that could be removed by a mechanical type of filter. For this reason, the most practical and economical procedure for filtering aluminium-rolling oils is to utilize, on a full-flow basis, a mechanical filter capable of removing impurities down to the smallest practical particle size, and call upon the absorbent-type filter to remove the impurities of extremely small particle size from the mechanically filtered oil.

6. Suggested Oils for Cold Rolling

(a) Copper.

For intermediate passes: 43–54 Centistokes at 100° F. (38° C.) mineral oil, preferably reinforced with film-strength and lubricity additives.

For finishing passes: 4–6 Centistokes at 100° F. mineral oil, preferably containing film-strength and lubricity additives.

(b) Aluminium.

For all cold rolling: 4–6 Centistokes at 100° F. mineral oil, containing film-strength and lubricity additives. (For large-capacity recirculation systems, the addition of an oxidation inhibitor may be necessary.)

The suggested additives might be selected from the following, either singly or in various combinations, to suit varying operating conditions :

Film strength improvers :	Organic phosphorus compounds.
Lubricity improvers :	Synthetic esters.
	Fatty oils.

II.—PRESS DRAWING.

Press drawing is one of the most important of the many cold-working operations and includes those processes by which sheet metal is substantially and permanently deformed without rupture by the application of tensile forces. The working of the metal to a new shape is accomplished in the plastic flow range of the metal being formed.

1. *Lubrication Requirements for Drawing Operations.*

Drawing operations and the mechanisms involved suggest the desirability of using drawing lubricants of maximum film strength and, in most cases, maximum lubricity. Maximum film strength contributes towards the elimination of seizure or welding by effectively separating the surfaces of the tool and the work; maximum lubricity enables the metal to be drawn with minimum pressures and power. In general, the lubricants used should accomplish these ends with a minimum loss of die metal due to abrasives or to reactive materials incorporated in the drawing lubricant.

In choosing a drawing lubricant, numerous factors other than the actual drawing operation must be considered. One of the most important of these is the subsequent processing of the drawn parts; other factors are the method of lubricant application, ease of mixing or other preparation required, odour, &c. Drawing lubricants which meet these additional demands may well have to compromise with the optimum of high film strength, high lubricity, and minimum abrasiveness.

An examination of the various drawing operations and their comparative lubrication requirements will indicate where a necessary compromise in lubricating qualities can be tolerated, in order to make the lubricant suited both to the drawing operation and any subsequent processing.

(a) *Drawing of Cylindrical Parts.*

In drawing cups or shells, even in deep drawing, there will be very little ironing, particularly where the die clearance is sufficiently generous. In these cases the wall metal of the drawn shape merely becomes slightly

thicker. In such operations, maximum lubricity is desirable in order to reduce friction at the holding-down pad and at the die edge, and compounded oils are necessary. If, however, the draw is shallow and the metal thin, an ordinary straight mineral oil may suffice.

When ironing is appreciable, as it well may be, towards the end of a deep draw, an oil containing a high film-strength additive will probably be essential. In such cases, although highly surface-active anti-welding additives may function successfully as a drawing lubricant, it may be necessary to make use of one of the many mechanical spacing materials or fillers.

The deep drawing of cylindrical parts involving some ironing can be considered to have two distinct lubrication phases. In the early part of the draw, before ironing is appreciable, it is desirable to have high lubricity and low friction; in the latter part of the draw, where ironing should preferably take place, it is essential to have a film-strength or anti-welding characteristic in the lubricant, even at the expense of lubricity if that becomes necessary.

(b) Drawing of Rectangular Parts.

The conditions that apply in regard to the desirable characteristics for cylindrical parts apply also to square and rectangular shapes. Generally, any ironing towards the end of a rectangular draw is unlikely to be as severe as with cylindrical shapes, because of the escape afforded to the thickening metal by the unstressed sides. The film strength of the lubricant required may therefore be slightly less than when drawing deep cylindrical parts. However, a high degree of lubricity still remains desirable.

There is another aspect of the lubrication problem in drawing rectangular parts of large size. If it is practical to lubricate the corners, and not the sides, metal flow may be effectively controlled. The lubricant applied to the corners assists in correct metal flow; at the same time, the absence of lubricant on the sides helps to maintain the restriction of the metal in the unthickened sides, which, if not well restrained, tends to run into the die cavity too quickly. For local application, the lubricant should have sufficient immobility to remain in position and not to run to parts of the blank where it is actually a liability.

(c) Ironing Operations.

In an ironing operation to effect a reduction in wall thickness, as contrasted with ironing to effect polishing or exact sizing, exceptionally high film strength is essential, and lubricity is of only secondary im-

portance. The conventional extreme-pressure, anti-welding materials are not always adequate in heavy ironing operations and may require the application of solid spacer materials, or of chemical film formers such as active sulphur, chlorine, or phosphorus compounds.

The ironing operation is so severe that certain metals are almost unironable, and even aluminium, which is normally comparatively easy to work, sometimes gives considerable trouble. Where heavy ironing operations are performed, it is desirable to have full-flow application of the die lubricant over the die, and even through the punch. This effort to achieve maximum cooling is, of course, a further concession to the severity of the operation.

(d) *Taper Drawing.*

The lubrication requirements for taper drawing differ from those for cylindrical draws. Taper drawing involves the use of high pressures on the holding-down pad to permit stretching of the blank between the punch face and the die-ring. The holding-down pad pressure may be far in excess of the amount required to prevent wrinkling in order to restrain the metal and bring about the desired stretching. Ironing also is sometimes performed in this area by suitable shaping of the draw area. A drawing lubricant possessing too high a degree of lubricity may reduce the holding force; accordingly, high film strength is required without too much lubricity.

In the less severe tapering operations, it may seem logical to use lubricants of higher lubricity, since less frictional resistance is required to control the operation. However, it is believed that lubricants possessing too high a degree of lubricity cause puckering of the sides of the shape.

(e) *Drawing of Large Irregular Shapes.*

As many simple drawing operations in large irregular shapes may be performed in the blank at one time, the lubricant selected must be chosen for the most severe of the individual operations. If, for example, a rectangular corner is being drawn to a depth which approaches the maximum for that radius, and other operations such as tapers and cylinders involve only a shallow depth, it would be necessary to choose a lubricant on the basis of the requirements of the rectangular draw.

One operation which invariably appears in the drawing of large irregular shapes is stretching over the male die. While the total force may be great on this area, the unit pressure may be quite moderate because of the large punch area. Accordingly, the film strength required is slightly lower than, for example, that required in ironed cylindrical cups. Here again, lubricity is relatively unimportant.

2. Influence of Subsequent Processing on Choice of Drawing Lubricant.

The subsequent processing which drawn parts have to undergo is often as important a factor in choosing a lubricant as the drawing operation itself. A lubricant that gives satisfactory results in the drawing operation, but which unduly complicates subsequent processing, such as storage, annealing, and cleaning, cannot be used.

Some types of drawing lubricant, unless removed immediately, stain the drawn parts while they are in storage or lying idle between operations. Such lubricants are generally unacceptable, except for rough work where staining is not objectionable. Simplification of processing often necessitates inter-stage annealing without previous removal of the drawing lubricant. This calls for a lubricant that will not stain under a variety of annealing conditions. Easy cleaning by a variety of procedures is a prime requisite of satisfactory drawing lubricants. The degree of cleanliness attained is difficult to define and can best be approached by considering the sensitiveness of the process to follow the cleaning.

3. Suggested Lubricants for Press Drawing.

There are so many different types of operation falling within the general category of press drawing that the tidy grouping of appropriate lubricants is not so simple as it is for cold-rolling operations. However, it may be stated broadly that, to comply with the requirements of complicated drawing operations on different types of metal, the severity of the draw should be related to the gauge of the metal blank and the extent of the reductions desired.

Although the following recommendation cannot be applied in detail, it forms the basis for making an appropriate selection according to the severity of the operation :

Mineral oils varying in viscosity from 43 to 220 Centistokes at 100° F. should be selected, the choice depending on the gauge of material and severity of the draw, and containing the following types of additive, either singly or in various combinations :

Film strength improvers :	French chalk.
	Sulphur compounds.
	Chlorinated materials.
	Organic phosphorus compounds.
Lubricity improvers :	Synthetic esters.
	Fatty oils.

III.—TUBE DRAWING.

The cold drawing of tubes is designed to produce tubing of a specified size, finish, and physical characteristics. Practically all types of metal

tubing are cold drawn, the most common of the non-ferrous metals being copper, brass, and aluminium. The drawing operation is performed on a draw-bench, which is essentially a suitable mechanism capable of pulling a comparatively long tube through a circular die. There are four principal methods of tube drawing, viz.: sinking, rod-mandrel drawing, plug-mandrel drawing, and floating-plug drawing.

1. Mechanical Factors Affecting the Choice of Lubricant.

The same basic mechanical factors that affect other cold-working operations apply also in tube drawing. The operation is, of course, performed above the yield point of the metal, and the extent of drawing is limited by the rate of work-hardening and the spread between the yield point and the ultimate tensile strength. These factors vary with the different metals and their condition.

The severity of the operation is generally measured by the percentage reduction in cross-sectional area of the metal. There is some doubt whether this is a completely satisfactory method, since it does not take into consideration the quantity of metal involved. It is reasonable to expect that the pressures involved in reducing thin-walled tubes may differ considerably from those involved in effecting the same percentage reduction of thick-walled tubes. Since there is, as yet, no satisfactory method of correlating the quantity of metal moved with the percentage reduction in section, it is wise to note in every operation the inside and outside diameters, both before and after drawing.

The actual method of drawing—by sinking, rod mandrel, or plug—is also an important factor. Sinking is probably the least severe and the possible reduction is limited only by the tendency of the metal to wrinkle. Rod-mandrel drawing doubtless creates the highest pressures, principally because this method is used only when large reductions are desired. Plug-mandrel drawing probably creates pressures intermediate between sinking and rod-mandrel drawing, but lubrication may be more difficult because of the inaccessibility of the plug.

The speed of drawing also affects the operation, being a major factor in the heat build-up. An allied factor will be the facilities provided for easing the shock at the beginning of the draw, by means of variable speed drives.

2. Application of Lubricant.

The method of application may severely limit the choice of lubricant. Full-flow application over the outside of the tube and the die requires a fluid-type product that is capable of circulating freely. Dip application at room temperature, or sometimes at an elevated temperature,

necessitates the use of a lubricant that will leave a durable coating on the work throughout the full period of the draw. Dip application of such a lubricant is the most practical method for lubricating plugs. In the case of plug-mandrel drawing, it is possible to provide for force-feed lubrication by forcing the lubricant up the rod, but for floating-plug drawing there is no practical method of employing this type of application. Swab or hand application of heavy-bodied lubricants is the method normally used to apply lubricant to the rod in mandrel drawing, or to the plugs in plug drawing. In addition, swabbing of the die and tube is the normal practice of applying the lubricant externally.

Actually, rod lubrication is primarily a separating or a parting problem, since there is comparatively little relative movement between tube and rod as they are pulled together through the die.

3. Influence of Drawing Lubricant on Subsequent Processing.

Although operations subsequent to tube drawing do not as a rule severely limit the choice of lubricant, there are some factors which must be given consideration. In those cases where the tubing is cleaned before annealing, the characteristics of the lubricant must permit removal without injury to the metal surfaces. Where no cleaning operation is performed before annealing, the characteristics of the lubricant must be such that it will burn off cleanly without leaving permanent stains.

4. Factors Influencing the Choice of Lubricant.

There are so many variable factors which influence the choice of drawing lubricant that it is not possible to make an outright selection without giving due consideration to the varying conditions. This can be appreciated from the following list of variables that exist in tube-drawing operations: (1) Type of metal (copper, brass, aluminium, &c.), (2) condition of metal (fully annealed or work-hardened), (3) size of tube, (4) method of drawing (sinking, rod-mandrel, or plug), (5) drawing speed, (6) severity of draw (percentage reduction), (7) method of application (force feed, dip, or swab), (8) subsequent operation (cleaned or annealed without cleaning).

5. Suggested Lubricants for Tube Drawing.

In copper tube drawing perhaps the best results are obtained with either soft lead-base greases or viscous leaded oils, but because these materials are not too easily removed they have certain disadvantages. Alternatively, partially water-soluble pastes or very viscous mineral oils can be used as a compromise. On automatic draw-benches, when

flood application to the plug and die is made, the oil viscosity is limited by its pumpability.

In aluminium tube drawing, conditions are generally much less severe and the use of a viscous mineral oil should suffice.

For copper, mineral oils of viscosity 170–220 Centistokes at 100° F., containing either one or several of the following additive materials may be used :

Film strength improvers :	Metal soaps. Chlorinated materials. Organic phosphorus compounds.
Lubricity improvers :	Synthetic esters. Fatty oils.

IV.—WIRE DRAWING.

Wire drawing involves the progressive reduction in section of metal rod or wire as it passes through a series of dies. Circular sections are most common, but other shapes are produced by this method.

After the first heavy reduction, generally on heavy bull blocks, the wire is usually drawn in multiple-die machines in which the wire may be reduced to a diameter as small as 0.05 in. If further reductions are necessary, the work is continued in special fine-wire machines.

1. *Mechanical Factors Affecting the Choice of Lubricant.*

The basic mechanical factors in wire drawing are similar to those already described. Since the operation must be performed in the plastic-flow range (above the yield point) the work-hardening tendency and the spread between yield point and ultimate tensile strength of the metal are primary considerations.

The severity of the operation in any instance is measured by the percentage reduction in cross-sectional area. This reduction may be as high as 50% in a single-die machine, but the reduction per die in multiple-die machines is usually less. Drawing speed is important since it directly influences the amount of heat generated.

2. *Application of Lubricant.*

Various methods of lubricant application are employed. Most of the slower-speed machines have no facilities for full-flow application of die lubricants. Instead, they have a soap box before each die, in which the lubricant is placed and through which the wire passes into the die. Most intermediate and fine-wire machines have facilities for flood lubrication of the dies. This is accomplished either by a circulation

system that delivers a full stream of lubricant to each die, or by submerging the entire die assembly in a bath of lubricant.

Each of these methods of application makes particular demands upon the lubricant. The soap-box method requires a lubricant that will adhere strongly to the wire since, in some cases, it must suffice for a number of dies. The lubricant used in a circulation system must be chemically stable enough to resist the oxidizing influences of air, high temperature, and the catalytic effects of the metallic dust with which it becomes contaminated.

Other factors affecting the choice of a wire-drawing lubricant are the operations subsequent to drawing. Staining of the wire in storage, staining during various annealing processes, and washability are often factors to be taken into account.

3. Drawing of Copper Wire.

Copper wire is usually drawn with soap-in-water solutions, or with a mineral oil containing load-carrying and lubricity additives. These are used in varying concentrations in rod, intermediate, and fine-wire machines, and the lubricant is generally applied by full flow to the dies. In the relatively slow drawing of copper rod, mineral oils containing fatty or chemical lubricity additives give satisfactory results.

Experience in intermediate and fine copper wire drawing indicates that the operation is very sensitive to the lubricity and tackiness characteristics of the wire-drawing lubricant. Either too little lubricity or too great a tackiness may cause fine wires to stick to the rolls or feed too rapidly to the dies, resulting in snarls and breaks. Too great a lubricity may cause the wire to feed too slowly to the dies, which results in the wire pulling apart. The lubricity requirements can usually be controlled by carefully varying the concentration of the lubricant used. The introduction of a new machine—particularly a fine-wire machine—calls for the application of trial-and-error methods to establish the characteristics suitable for the wire-drawing schedule employed.

4. Drawing of Aluminium Wire.

Aluminium rod and heavy wire are generally drawn with mineral oils containing fatty additives. Fine-wire drawing of aluminium is comparatively new and both mineral oils and water-soluble oils are used. In general, the use of water-soluble oils is of questionable value because of the tendency towards staining which is encountered when aluminium is worked in the presence of water.

5. *Suggested Lubricants for Wire Drawing.*

For wire-drawing operations, the following might be regarded as appropriate selections :

Copper :

(a) Mineral oil of viscosity 45 Centistokes at 100° F., containing film-strength and lubricity additives, for drawing speeds below 1000 ft./min. (b) Mineral oil of viscosity 21 Centistokes at 100° F., containing film-strength and lubricity additives, for speeds above 1000 ft./min. (Where heat removal in high-speed drawing creates a problem, soap-in-water emulsions must be used.) Appropriate additives are as follows :

Film strength improvers :	Chlorinated materials.
Lubricity improvers :	Fatty oils.

Aluminium :

(a) Mineral oil of viscosity 170–220 Centistokes at 100° F., containing fatty oil, for drawing speeds up to 1000 ft./min. (b) Mineral oil of viscosity 10–20 Centistokes at 100° F., containing fatty oil, for speeds above 1000 ft./min.

6. *Treatment of Wire-Drawing Oils.*

The problem of removing aluminium fines in cold-rolling operations (see p. 489), applies in a somewhat similar measure to lubricants used for aluminium wire drawing, but, because many of the lubricants used in the latter process are much more viscous, filtration of the lubricant presents a much greater problem.

So far, filtration of aluminium wire-drawing lubricants has not been tackled on a continuous basis, but it is believed that, in order to produce acceptable wire and eliminate one of the sources of over-heating, this problem must ultimately receive attention. Because the production of aluminium wire is a relatively new industry, the correct technique has not yet been developed. At this stage it would appear that the process is regarded as just another wire-drawing operation and it is assumed that the principles that apply to brass and copper apply also to aluminium; consequently, the same lubrication arrangements found acceptable for the former operation have been adopted for the latter.

It is believed that the removal of contaminants from aluminium wire-drawing lubricants could be effected in several ways :

(1) The small drawing-oil capacity that is provided on most existing machines necessitates rapid recirculation of the lubricant. Because of this, the lubricant is in a state of continuous agitation and no opportunity exists for the precipitation of contaminants. This condition

could be relieved by increasing the drawing-oil capacity to provide for a much longer settling time.

(2) At least some of the contaminants present in the oil would be of a particle size which could be removed by fine mechanical filtration. Obviously such a filtration procedure should be on a full-flow basis.

(3) It is appreciated that the complete removal of contaminants can only be achieved by earth filtration. This presents obvious problems in so far that existing lubricants : (a) are quite viscous and consequently the filtration rate would be low, and (b) normally contain fatty materials which would be removed by the filtering medium. Problem (a) could be overcome, but this would necessitate the introduction of two heat-exchangers—one to heat the oil in order to reduce its viscosity to permit more rapid filtration, and one to cool it before application to the dies. Problem (b) would be unlikely to be solved by heating before filtration, but this would contribute towards a reduction in the removal of the fatty-additive content.

The ultimate solution to this problem may lie in the production of a compromise lubricant of lower initial viscosity, whose load-carrying and lubricity characteristics had been enhanced by the use of suitable chemical additives. Such a product should permit filtration without pre-heating, and the chemical additives should resist removal by the filtering medium.

V.—GENERAL CONCLUSIONS.

The lubricants recommended as appropriate for the various cold-working operations represent a broad guide only, and they should not be regarded as the only types of lubricant that will give satisfactory results. In fact, there is much room for improvement in performance, which it is believed can be achieved only by much closer co-operation between the cold metal-working and petroleum industries.

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THE COLD ROLLING OF NON-FERROUS METALS IN SHEET AND STRIP FORM.* 1288

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SYNOPSIS.

After reviewing recent progress in rolling practice, the author describes modern technique in rolling: (a) copper and copper alloys, and (b) aluminium and its light alloys. The relative merits of two-high and four-high mills for various purposes are described, and also those of reversing, non-reversing, and tandem units. Reference is made to the latest designs for mills with minimum work-roll diameters, such as the Sendzimir mill. Considerable attention is given to the auxiliary equipment required to handle sheet and strip during rolling.

I.—INTRODUCTION.

As it is impracticable to deal with the cold rolling of all non-ferrous metals in this paper, its scope will be limited to the production of cold-rolled sheet and strip in the two classes of material which form the bulk of the output of the non-ferrous metal mills: (a) copper and copper alloys, and (b) aluminium and its light alloys.

Although plant employed and the technique practised differ in these two cases, they have many features in common. In the copper alloy group, brass is of the greatest importance. In the aluminium and light metal group there is a wide range of material from pure aluminium to the strong alloys of the Duralumin class.

The brass industry is far older than the light-metal industry; the latter is of comparatively recent establishment, and its development has consequently been greatly facilitated by starting at a later stage in the progress of rolling-plant design and practice. On the other hand, with brass, old-established works, generally relatively small units, have been handicapped by the existence of old and semi-obsolescent plant and to some extent by the traditions of old practice and craftsmanship.

The chief differences in rolling technique, and plant employed, are basically due to metallurgical and physical reasons; for example, as copper alloys have on average a specific gravity about 2.5 times that of the commoner aluminium alloys, the bulk of the latter and the superficial area of strip or sheet produced from an ingot of given weight are correspondingly greater than those from a brass ingot of similar weight.

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The practice in cold rolling light metals has been largely modelled on that developed for the rolling of mild steel, where the trend has been towards an ever-increasing weight of ingot and consequently of heavy coils in strip rolling. In the early days of the brass industry the ingots were very light (80–100 lb.), and although recent progress has led to the casting of ingots up to 2000 lb. weight (3000 lb. is becoming a practical proposition in America), there has been a similar increase in light-alloy ingot weights, ingots of 2000 lb. and over being already cast and handled, and the most modern aluminium mills in this country are designed to handle much heavier slabs still.

There is another difference arising from the fact that while from the beginning of the rolling of aluminium and its alloys the breaking-down process from ingot has been carried out at “hot” rolling temperatures, brass—in most qualities—has been cold rolled from ingot, and still is in many works both large and small; and it is only recently that the hot breaking-down process has been largely adopted for a wide range of alloys. Physically, therefore, in the cold rolling of brass from the ingot the thickness of the cast slab is for obvious reasons limited. Incidentally, the cold breaking-down of brass ingots appears to be largely preferred in America to hot breaking-down for reasons which will be explained later.

In discussing the cold rolling of the range of non-ferrous metals and alloys under consideration, it is necessary to refer to the previous hot-rolling process, and while in many cases the cold rolling of brass will start from the ingot, with light metals and alloys not only is the preliminary breaking-down process carried out on heated metal, but modern developments have also tended to carry the hot rolling so far as to eliminate a great deal of cold rolling which was formerly regular practice. It may be that in future the cold rolling of light metals will be limited to the few final passes such as are necessary to obtain the desired surface finish and accuracy to gauge.

In both classes of metals there are two main types of production : (i) large outputs of more or less standardized products; and (ii) smaller outputs in a great variety of products, differing in alloy composition, physical dimensions, and quantities. In both these classes progress has been prompted by the desire, and the need, for more economical production, requiring less labour and again—in all cases—for a more accurate product. This has been achieved in (i) above by using larger ingots, which make it economical to adopt higher rolling speeds, heavier reductions per pass, and the development of the four-high or backed-up roll mill, first as single units, reversing or non-reversing, and further in multi-stand tandem trains, together with improved handling methods

and equipment. This development has also resulted in the practice of rolling wide strip in coils for the production of sheets, as against the older method of rolling in sheet form.

In the progress outlined above, the improvements in design and construction of high-production and more powerful rolling plant by the mill builders have generally been capable of fulfilling the demands of the metal industry.

In the case of (ii) above, where the tonnage required in any one quality or dimensions is small, plant as indicated above, involving heavy capital expenditure, would obviously be uneconomical. Ingot weight is necessarily limited, and progress has been confined to the general increase in rolling speeds and more efficient rolling mills and auxiliaries. In a large establishment plant may be required of both types.

Some credit is due to the engineer, who with the help and co-operation of scientists has during recent years studied the mechanism of the deformation of metals by rolling and has developed more scientific means—although still largely empirical—for calculating roll loads and power requirements in place of the old rule-of-thumb methods, based largely on the experience of the practical roller working with inadequate and inefficient plant. By collecting and comparing data from actual works' practice and by independent experimental work, practical methods have been developed and improved so that for some time past it has been a relatively easy and simple matter to forecast the performance of mills and the power required for any specified duty with a reasonable degree of accuracy. The essential dimensions of mill components can also be determined on a logical basis.

One of the most important contributions to progress made by the engineer has been the development of more efficient roll bearings. There was little or no advance in rolling plant—and particularly as regards increased rolling speeds—until the problem of heavy frictional losses in the roll bearing was solved by the production of roller bearings capable of carrying the heavy loads common in any cold-rolling mill, and the later development of the fluid-film, oil-lubricated bearing both in this country and in the U.S.A. The fluid-film bearing with low-pressure circulation of ample volume of oil, which acts both as a lubricant and a means of carrying away the frictional heat, was first designed in this country and introduced in 1928. In America the first successful fluid-film bearing was produced and tried out in about 1931.

Before these vital improvements in the mechanical efficiency of the cold-rolling mill, the frictional losses in roll-neck bearings were quite normally as much as 50% of the total power absorbed by the mill, and in some cases as high as 90%. While recent tendencies have perhaps

favoured the film-lubricated plain bearing in its several forms, a considerable debt is due to the roller-bearing makers, as the use of this type of anti-friction bearing showed at once the low efficiency of the old-type bronze, grease-lubricated, bearing, and also directed attention to the need for the accurate measurement and determination of roll loads. With the old-type roll bearings high rolling speeds were practically impossible, owing to the excessive heat generated and the consequent loss of power, and for many years the opinion persisted in the rolling industry that cold-rolling speeds above about 100 ft./min. were uneconomical, if not impracticable.

Following the pioneer work in design and construction of efficient roll bearings, and the establishment of the fact that the power required in rolling was substantially proportional to the rolling speed—showing that the cost in power and maintenance per ton output in the operation of the mills was not appreciably greater at high speeds than at the old low speeds—there has been a general tendency towards increased rolling speeds.

In Sections II and III of this paper, the cold rolling of copper and its alloys, and of aluminium and its light alloys, are discussed separately ; but as, in spite of the differences in the rolling of these two classes of non-ferrous metals, there are very many common problems (and in some respects similar techniques), many general questions discussed and plant described in one section will apply equally to the other. Some cross-references may therefore be necessary.

II.—ROLLING OF COPPER AND COPPER ALLOYS.

Great progress has been made in copper and brass rolling during the last 25 years ; this advance has not only been in the installation and development of large modern plants, but also in the medium-sized and smaller mills for more specialized production in smaller quantities.

In both types of plants progress has been made in regard to : (i) increase in widths rolled, (ii) increase in weight of ingots, (iii) increase in rolling speeds, and (iv) installation of more modern and efficient mills and auxiliary equipment. At the same time there has been the demand of the buyer and user for better quality, surface finish, and accuracy of product.

1. *Breaking-Down.*

In the copper group brass in its several compositions forms the greatest part of the total production. Until comparatively recently the cold rolling of brass started with the ingot (except in certain hot-

rolling alloys); nowadays the hot breaking-down of ingots in a wide range of brass alloys has been increasingly practised in the larger mills, while the smaller plants have continued with cold breaking-down.

It is notable that in America cold breaking-down from ingot is adopted even in the largest and most modern plants. This is mainly due to the output of such mills having a large proportion of leaded brasses which cannot be successfully hot rolled; in one large mill 35% of the total product consisted of brass containing lead, and bronzes. In some cases in the United States a relatively large proportion of scrap metal, which may contain impurities such as lead, is used, which precludes hot rolling of many alloys.

Alpha alloys, such as 70 : 30 brass, can be readily rolled hot, but only if the composition is free from impurities. For large outputs the hot breaking-down mill would appear to have economical advantages over the cold process in requiring less power per ton of metal rolled and the elimination of annealing during the breaking-down stages of reduction.

In the smaller mills cold breaking-down is the most economical method, especially for those handling light ingots (250–300 lb.) with correspondingly small thickness. In America it has been possible to produce heavy ingots (2000–3000 lb.) with an economical thickness for cold rolling of about $2\frac{1}{2}$ in., by the development of the continuous-casting process, the required weight per ingot being obtained by increased length rather than thickness.

In the case of heavy ingots cast in water-cooled moulds of economical weight, the thickness must be 4–5 in., and for these hot breaking-down is the only practicable method. Copper is, of course, always rolled from ingots in the hot state. To meet all requirements, large plants in America and in this country have both hot and cold breaking-down mills.

The modern, non-reversing, cold breaking-down unit for ingots about 24 in. wide by $2\frac{1}{2}$ in. thick must be a very powerful mill, with rolls about 30 in. dia. and motor power of 1000–2000 h.p., and in production efficiency it can equal the hot breaking-down mill. A description of the powerful cold breaking-down mill in the new mill of the Scovill Manufacturing Co. at Waterbury, Conn., U.S.A., is given in the paper by Hoben and Mulvey.¹

A recent report on the observed performance of non-reversing cold breaking-down mills in the United States advises that batch-rolling 2000-lb. ingots, $2\frac{1}{4}$ in. thick, with pneumatic or hydraulic "stick-ing" device (to effect positive entry of the metal between the rolls) and with mechanical transfer of batches of ingots to the feed side for consecutive passes, 20 ingots were fed through the mill with no greater

interval than 12-18 in. between the tail end of one slab and the leading end of the next.

The final thickness of slabs after hot breaking-down is usually between 0.4 and 0.150 in. Copper is generally hot rolled to 0.150-0.180 in.; at these thicknesses cold rolling begins. In the case of cold breaking-down, this stage of reduction will generally bring the thickness down to about 0.4 in.

In this country, the hot breaking-down process is generally preferred for large productions, and in this connection the question of standardized width of ingot and strip produced has to be considered. The tendency has been to adopt a standard width of 24-27 in. and to continue rolling down in this width to normal finished gauges, it being obviously more efficient to roll in the maximum convenient width and to supply the demand for narrower widths by slitting—in cases where very light gauges are required—before the final finishing passes in narrower mills. It may be remarked that strip up to 1 m. (40 in.) is rolled. In certain Continental works, with relatively small production requirements, hot breaking-down is adopted with a standardized width of about 700 mm. (27.6 in.), but in Britain small and medium-sized works using cold breaking-down usually find it necessary to work with narrower ingots (7-16 in.), the maximum width being largely dictated by the size and power of the breaking-down mill available.

The question of the most economical standard maximum width is fundamentally important in determining the design of a modern brass mill. This standard width should be selected to cover the maximum width of finished strip or sheet required, and in the case of brass 2 ft. 0 in. would seem to be the average maximum required. Wider sheets (as may be required in copper) are then produced by cross rolling, as separate sheets.

2. Slab-Milling or Overhauling.

Excepting where surface condition is not of importance, it has been general practice for some time past to slab-mill or overhaul the surfaces of the slabs after the initial breaking-down, whether hot or cold, to remove the dirty surface metal. This machining process also has the advantage of removing surface defects, thereby not only improving the quality and appearance of the finished strip or sheet, but also minimizing the rejects and scrap loss in pressings made from the strip, particularly brass cartridge cases.

One of the most efficient machines for this process is the well-known Torrington slab-milling machine, which has been employed in America and in this country for many years past, and since the beginning of the

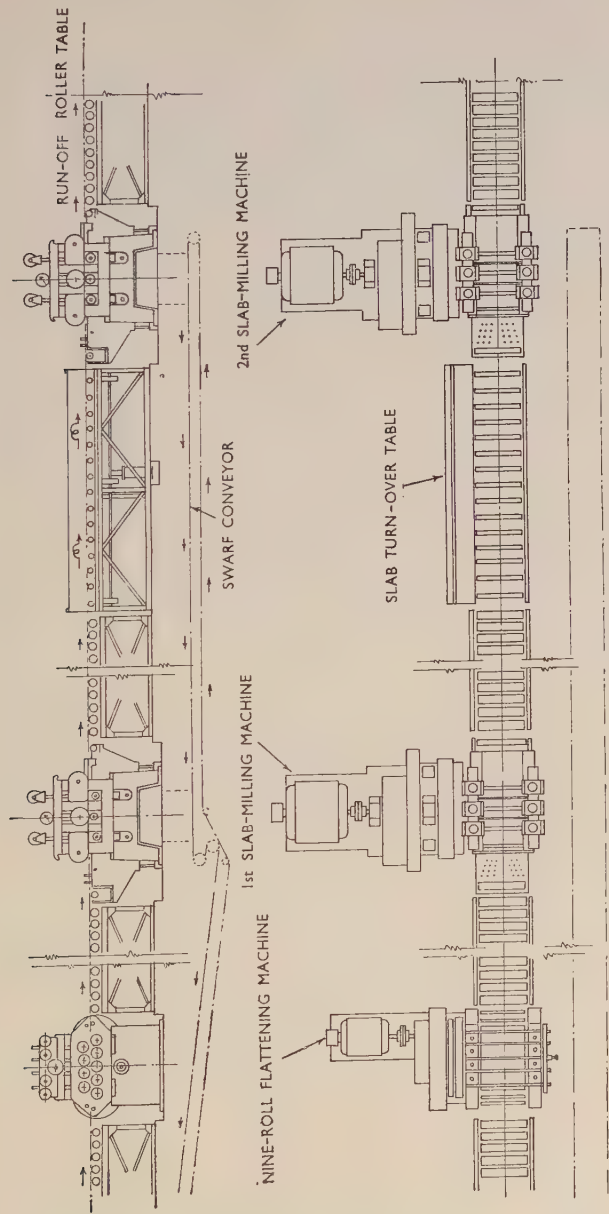


FIG. 1.—Arrangement of Slab-Milling Line.

last war has been installed in nearly all the leading brass mills in this country.

Before milling, the strip or slabs, whether coiled or in straight lengths, must be flattened, and a suitable multi-roll flattener followed by one or two slab-millers form a slab-milling line (Fig. 1). The milling machine itself has one or more pairs of power-driven feed rolls at each end that pass the slab over a high-speed spiral milling cutter, above which an adjustable backing roll is mounted so that the depth of cut can be regulated. Only the underside of the slab is machined in one pass, and consequently for large outputs two machines may be installed in tandem with a turn-over table between them, so that the metal is flattened and milled on both sides in one continuous operation. For small outputs one miller only need be installed, with mechanical means of transferring batches of slabs back to the entry side, and a turn-over table for the second pass to complete the milling of both sides. The older standard machines for strip up to 16 in. wide were usually run with a fixed feed speed of about 18 ft./min., but later designs taking slabs up to 30 in. wide are now in use, and still wider machines for 40-in.-wide metal are being constructed. As the maximum feed speed ranges from 15 to 30 or even 45 ft./min., depending on the quality of metal milled, the most modern slab-millers have separate variable-speed motor drives to the feed rolls and cutter, so that both feed and cutting speed can be adjusted to those most suitable to the particular metal handled.

Slabs are usually milled at a thickness of 0.4–0.6 in., but when required—in the case of hot-rolled strip—a minimum thickness of $\frac{1}{4}$ in. can be milled. Most non-ferrous metals can be milled, including nickel alloys, brass, and copper, and where strip is required to be milled in coils a roll-type up-coiler can be added to the train and the coils can be processed in batches, being decoiled by the flattening rolls after the first pass and re-coiled after the final run through the line. The depth of cut taken on each side will range between 0.010 and 0.020 in.

The machines are so designed that the chips fall under the machine, where a mechanical conveyor can be provided to carry the swarf away and load it into bins or wagons. Large plants are now equipped with a pneumatic swarf-removal system by which the chips are sucked or blown through pipes leading to any convenient storage for remelting.

3. Sheet Rolling.

It is perhaps useful to consider here the older practice of rolling copper and brass in sheet form, although this has been largely superseded by the cold rolling of wide strip in coils, which is finally flattened

and cut to the required sheet lengths. Generally, the practice in sheet-rolling is to take strip which is narrower than the required width of the finished sheet and which has already been reduced by previous rolling as strip, to a convenient thickness such as $\frac{3}{16}$ or $\frac{1}{4}$ in., shearing it to lengths which correspond to the required finished width of sheet, and cross-rolling it to final gauge, i.e. rolling in a direction at right angles to the original direction of the initial strip-rolling.

Until about 20 years ago this final sheet-rolling was done in two-high mills, with rolls 24–28 in. dia. and with a barrel length of 5 ft. 0 in. or so, the sheets being returned over the rolls for successive passes; owing to the unavoidable deflection of the rolls, and the necessity of maintaining flatness and freedom from “buckles”, a very great number of passes were necessary to effect the total reduction to finished gauge.

A considerable advance was made by the introduction of the four-high sheet mill; this, by virtue of the smaller diameter of the work-rolls (12–17 in.) with the support against deflection by the larger backing-rolls (24–42 in. dia.) drastically reduced the number of passes necessary. Where the old two-high mill would require 20–50 passes (depending on the finished gauge) to reduce from sheet blank, the four-high mill effected the same reduction in 3–8 passes.

From another point of view the four-high mill has an advantage over the two-high mill for sheet production, in that a closer uniformity of gauge across the width of the metal is obtained; on wide sheet the two-high mill requires large-diameter rolls to minimize flexure under load, with a heavy camber, which in turn requires a carefully graduated pass schedule, for, as is obvious, rolls with any particular camber can give uniformity of gauge across the width of strip for all passes only if the roll pressure is approximately the same for each pass.

As will be mentioned later, even with the more rigid work-roll support, such as is provided in a backed-up roll mill, some camber is usually necessary, for besides roll flexure it is necessary to compensate for roll flattening, especially when rolling to light gauges; but with backed-up, small-diameter work-rolls the camber necessary is very small in relation to the face width of the roll, and will give a very uniform gauge across the width with quite appreciable variations in roll pressure.

Generally, with the four-high sheet mill, the reduction per pass which can be effected is not limited by the strength and power of the mill, but by the need to avoid “gathering” or pinching, that is, to produce a sheet which is a good “shape” and reasonably flat. It is, of course, obvious that with a four-high mill rolling sheet the method

of batch-rolling must be employed, as it is not possible to return the sheets over the mill to the entry side after each pass; consequently an efficient means of handling the sheets is required.

To facilitate the entry of the sheets between the rolls with a heavy reduction, power-driven feed-rolls are frequently fitted at the entry side. By this means the roller can easily introduce the sheets between the feed-rolls, which feed the sheets forward and provide sufficient power to force the leading edge of the metal between the mill work-rolls, even when these are set closely together in order to take a heavy pass reduction. Owing to the fact that in sheet-rolling the actual rolling time is unavoidably a relatively small proportion of the total time for handling and rolling each sheet, in economical production it is necessary to reduce the number of passes for any given total reduction to a minimum. This requires not only a heavy and rigid construction of the mill with stiff supporting rolls to minimize stretch and flexure of the mill components under load, but also the reduction of clearances and of any drop of the rolls after the sheet leaves the rolls to the minimum.

Even with the most robust design of mill housings and other loaded parts, an appreciable spring or total extension of the roll stand is unavoidable owing to the considerable length of the stressed housing limbs; on this account an increase of roll diameters, dimensions of housings, &c., will not reduce the total spring as much as would be expected, for the reason that with the increase of the roll diameters, &c., the total height of the mill frame is correspondingly increased and the total stretch or extension is greater. This factor becomes of greater importance with the harder metals and alloys. Even with very rigid construction the rolls may have to be pressed together with an appreciable preload before receiving a relatively thick sheet if a heavy reduction is required; under such conditions the total yield of the roll assembly may be 0.050 in. or even more.

Apart from spring or stretch, for maximum pass reductions, as indicated above, any movement of the rolls apart on the application of load, i.e. on entry of the sheet, must be minimized by providing adequate balancing, and indeed over-balancing, of the top working and support rolls, with their bearings, chocks, &c. This is most effectively obtained by hydraulic balancing cylinders, with rams fitted in the chocks, which will hold the upper roll assembly in close contact with the adjusting screws, with constant and adequate pressure, thereby taking up all bearing and other clearances. This condition is most important when rolling relatively thick metal, as in the first passes on the sheet blanks. At the same time care must be taken to avoid excessive balancing

loads between work-rolls which would bend the relatively small work-roll necks.

The other limitation to the amount of reduction possible in sheet-rolling, namely, the necessity to avoid "gathering" or pinching of the sheets as they pass between the rolls, may be countered by the provision of a device, usually called a "billy-roll" (Fig. 2). This equipment consists of a free-running roller, carried on fixed bearings under which the sheet passes, and between this and the mill rolls a second roller, ambushed in the feed table below the pass line, is arranged so as to be moveable upwards and towards the mill rolls by the action of a pneumatic cylinder. Directly the leading edge is gripped in the mill rolls, a valve is operated which forces the lower roller upwards, thereby bending the sheet and tending to wrap it round the upper work-roll. This action both flattens the sheet as it enters the roll gap and holds it taut by applying some degree of back-tension. The billy-roll, although it has been fitted to four-high mills and used by some steel-sheet rollers, has not been adopted generally in this country.

As previously mentioned, with sheet-rolling in a four-high mill batch-rolling is employed, and the handling and transport of the sheet to and from the mill are important factors in economical production. Stacks of sheet blanks of convenient weight are usually brought to the entry side of the mill on floor bogies, from which the operator feeds to the mill feed-rolls one by one. On the outlet side a belt conveyor (Fig. 3) is provided to carry the sheets from the rolls to a stacking table or transport bogie. The outer end of the belt conveyor is adjustable by an electric motor for height to suit the increasing height of the stack of sheets. The batch of rolled sheets can be transferred on the bogie from the outlet side of the mill in readiness for the second pass, and the operation repeated.

The tandem rolling of sheets has been adopted in several American mills; in this method of rolling sheets are passed continuously through

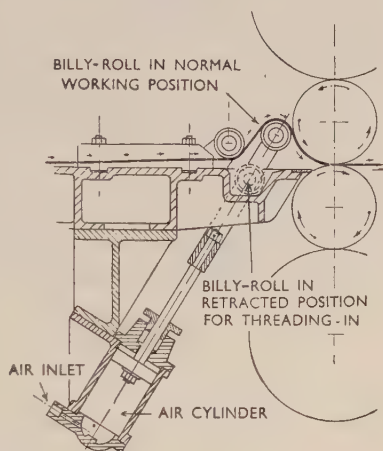


FIG. 2.—Arrangement of Billy-Roll for Four-High Sheet Mill.

three or more stands of four-high rolls, each stand being adjusted to effect the correct reduction. Where output requires several mills the tandem arrangement has a high productive efficiency. As sometimes there is a difficulty in entering sheets which have the leading edge sheared square into a mill with rolls set for maximum reduction, the practice adopted in at least one American mill, of shearing the ends of the sheets at a slight angle so that one corner of the sheet is first gripped by the mill rolls, is worth consideration. In large works, no doubt, the practice of sheet-rolling as opposed to strip-rolling may be considered as

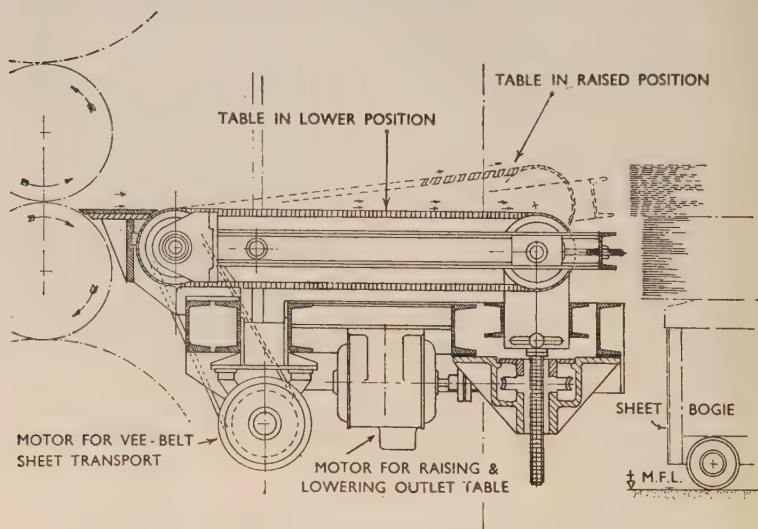


FIG. 3.—Arrangement of Outlet Table for Four-High Sheet Mill.

becoming obsolete and replaced by the continuous rolling of wide strip in coils in tandem continuous trains or reversing mills and, as already stated, in some modern mills 24-40-in.-wide sheets are rolled as strip, which is afterwards flattened and cut to required lengths. But in smaller establishments, handling a large variety of widths, qualities, and gauges with no great tonnage of any one sort, sheet-rolling is the only economical method, and in such cases the single-stand, non-reversing, four-high sheet mill will continue to be employed.

4. *Strip Rolling.*

Generally, modern practice in all strip mills is to instal a small number of powerful high-production mills equipped with the most efficient ancilliary and handling devices, each unit designed to deal with

one stage in the series of reductions from the raw material to the finished product, in place of the older method of a greater number of smaller and less powerful mills, as this results in the greatest economy in labour. In addition to these principal production units, it is usually necessary to provide a proportionate number of special-purpose mills, especially those for rolling to light gauges in narrow strip widths.

The modern brass-strip mill, for a large output in standard widths, after the breaking-down mill (either for hot or cold rolling), depends largely for further cold rolling to finished gauges on several four-high mills, each designed to effect a particular pass or passes, and it seems that generally, in this country at least, non-reversing mills have been preferred. Some 18 years ago Imperial Chemical Industries, Ltd., Metals Division, installed at their Witton works what was then a most modern plant; the hot breaking-down mill was a powerful reversing mill with edging rolls, roller tables, coilers, &c., and the cold mills initially consisted of: (1) a heavy, non-reversing, four-high mill, capable of effecting a heavy reduction on the strip supplied by the breaking-down mill, having a work-roll diameter of about 15 in., and (2) a three-stand, four-high tandem mill with smaller work-rolls (about 12 in. dia.). With these two units it was planned to finish strip ranging from 0.020 to 0.015 in. thick. Later other mills, both two-high and four-high, were installed, including a four-high reversing mill with still smaller work-rolls for finishing strip down to 0.010 in. In all the above-mentioned mills a standard strip width of 26 in. was handled. To obtain narrower and thinner strip, the wide metal from these bulk-production units was slit to the required narrower widths and reduced to light gauges in two-high and four-high mills with automatic coiling equipment and higher rolling speeds.

As will have been noted from the paper describing the new Scovill plant,¹ the number of mills installed there, also designed for about 25 in. width, was reduced to a minimum and consists of: (1) one heavy cold breaking-down mill, rolling ingots $2\frac{1}{2}$ in. thick to about 0.4 in., after which the strip is annealed and overhauled; (2) one "getting down" four-high, non-reversing strip mill, taking strip at about $\frac{3}{8}$ in. and reducing it to 0.05 in. thick; (3) one four-high finishing mill for normal-gauge production down to 0.011 in., also non-reversing; and (4) for light gauges, after slitting to narrower width, a non-reversing four-high mill of special design.

Another example of American practice is indicated by a proposal to instal in connection with existing plant: (a) a four-high reversing mill for brass and copper strip 25 in. wide, to reduce from 0.030 to 0.014 in. with a maximum speed of 700 ft./min. and (b) one reversing

four-high mill, with specially small work-rolls, in which the support rolls are driven, for light-gauge production in full-width strip, and capable of reducing from 0.014 to 0.002 in.

From the above it will be concluded that the four-high mill, either single-stand, reversing or non-reversing, or in a tandem arrangement of several stands, is generally adopted as the standard cold-rolling mill in a modern non-ferrous strip or sheet mill, certainly in the larger establishments in this country and America. Even in the medium-sized and smaller plants, of which there are many in this country still operating a large proportion of two-high mills, many four-high units have been installed in recent years.

Fig. 8 (Plate LIII) illustrates a heavy non-reversing four-high running down and finishing mill for wide brass strip, with work-rolls 15 in. dia., and support rolls 37 in. dia. with 60 in. face width, capable of rolling strip up to 48 in. wide. This mill is driven by motors through hydraulic variable-speed gear, giving 450 h.p., with variable rolling speeds up to 200 ft./min.

The mill is equipped with a roll-type up-coiler, with "tailing" device for coiling the thicker strip, this being designed to swing clear when not required, and a drum coiler for dealing with the thinner metal. This drum coiler is also driven by a separate motor through variable-speed gear with automatic tension control. Powerful two-motor screw-down gear is provided, which is capable of fine adjustment of roll setting under the heaviest loads.

Another four-high strip mill is illustrated in Fig. 9 (Plate LIV); this is a reversing mill with drum coilers on both sides and has work-rolls 12 in. dia. and support rolls 30 in. dia., and 34 in. face width; it is designed for finishing brass strip up to about 26 in. wide. The rolling speed is moderate (200 ft./min.), and the mill is driven by a motor of 400 h.p. The convenient arrangement and position of the controls for the main motors, two-motor screw-down, coil ejector, &c., will be noted.

The question arises as to whether there is still a place for the two-high mill in its latest form. For specially good finish it is reasonable to expect that the two-high mill, with rolls of correct proportions, which can perhaps be more easily maintained in a well-polished condition, may be preferred to the four-high mill. Indeed, in many plants with a moderate output and varied product, rolling a maximum width of about 15 in., two-high mills form the greatest proportion of the plant, in such cases following a cold breaking-down, with roll dia. 22-30 in. The "getting-down" unit may be an 18 in. two-high mill with ample motor power and a reasonably high speed, getting ready and finishing being

accomplished in a series of smaller mills with rolls ranging from 16 to 14 in. dia. for wider strip, to 12 and 10 in. dia. for narrower metal. Such mills will be operating as non-reversing units at speeds which once were considered high—250–300 ft./min. For “temper” rolling, where reductions per pass are less than 20%, the two-high mill is very efficient.

The two-high mill with rolls of larger diameter than the corresponding four-high design is useful as a general-purpose mill, and owing to the larger roll diameter will effect economical reductions on metal with a greater initial thickness; while the four-high mill with its smaller working rolls will show greater efficiency as the gauge is reduced. More generally the advantages of the four-high mill become greater as the ratio strip width/thickness increases. For the finishing of light-gauge strip in copper or brass—so long as this is rolled in relatively narrow width from 6 to 10 in., starting with metal already reduced to, say, 0.03 in. and rolling to 0.005–0.004 in.—the two-high mill with 10- or 12-in.-dia. rolls is an efficient machine, but for maximum production (with a minimum number of passes) several intermediate anneals are generally necessary with a total reduction of 0.03 to 0.004 in. in thickness. The four-high mill with smaller working rolls (not more than 5–6 in. dia.) will reduce the number of intermediate annealings, with a considerable economy in overall conversion costs. Again, if it is desired to produce strip thinner than 0.004 in. in any considerable width, the mill with small-diameter backed-up work-rolls is essentially superior, especially with harder alloys such as bronze and nickel silver.

There seems to be a considerable difference of opinion as to whether strip-finishing mills should be reversing or non-reversing. Recent American practice tends towards the use of non-reversing mills, in which case the batch-rolling system must be adopted, that is to say, a convenient number of strips or coils are handled one by one in successive passes. This involves the provision of efficient mechanical-handling equipment to bring the batch of coils after each pass back to the feed side of the mill. Any such conveyor system must provide room for the storage of a convenient number of coils.

The advantage of this one-way rolling mill over the reversing mill is that, when the rolls are correctly set for any reduction, a considerable number of coils are rolled without the delay in adjusting rolls after each pass, as is the case with the reversing mill. With proper mechanical-handling equipment, a high productive efficiency can be obtained by this method. Incidentally, the non-reversing mill involves an appreciably lower capital cost, particularly in regard to the electrical equipment.

The reversing mill, on the other hand, has the advantage of providing heavy and controlled back-tension, at least after the first pass; on this account a reversing mill may, on balance, be preferred for rolling heavy coils of wide strip to lighter gauges. But it is doubtful whether there is any advantage in reversing from the point of view of productive efficiency, as although there is less handling of the coils there is the unavoidable loss of time in resetting rolls and adjusting guides, and in reversing the direction of rolling.

With the non-reversing mill any back-tension is usually provided by means of some form of press, generally air-operated. In this connection it may be remarked that while in cold rolling light alloys the roller bridle in various forms is employed to provide back-tension, the device has not been adopted to any extent in brass and copper rolling. The combination of the roller bridle with an expanding-drum decoiler, with which some braking effect is provided, will give adequate back-tension and flattening effect at entrance to the mill rolls.

It is also doubtful whether a heavy back-tension in a strip mill has any appreciable advantage in decreasing the roll load for any given reduction, but some tension is necessary in order to control the strip as it enters the mill rolls and hold it flat, particularly with light gauges. The old practice of driving a wooden wedge under a bar and on to the strip between the entry guides has this object, i.e. both holding the metal flat and providing some back-pull.

With regard to the third alternative of continuous rolling in tandem trains of three or more four-high stands, such plants as are installed in many of the larger brass mills in the U.S.A. can be economical only where coils of considerable length are handled and for the mass production of strip in standard widths and gauges, so that the mill can be kept in continuous operation and the maximum speed maintained over a very large proportion of the strip length.

As in the case of the non-reversible, single-stand mill, the tandem mill requires no change in roll setting for any given total reduction and so tends to uniformity of gauge. On the other hand, for flexibility in changing alloys, width, and gauges, the single-unit mill has the advantage, and some even hold the opinion that a greater output is obtained per man with a number of independent stands than with the same number of stands in tandem.

Tandem mills cannot be considered for the smaller plants, especially those dealing with a great variety of product and handling coils of limited weight.

All forms of backed-up roll mills have for their object the reduction in the diameter of the work-roll, as the roll load—or pressure—is, for

geometrical reasons alone, thereby reduced; moreover, the height of the "peak" of the "friction hill" is reduced by decreasing the work-roll diameter. This in itself may not be of great practical advantage, but as the smaller the roll the less is the lateral spread, a greater total reduction before annealing is necessary can be taken without causing edge-cracking; this advantage is important with harder metals and alloys, and also when effecting reductions of softer metals which have been work-hardened to a high degree.

With the normal four-high mill the minimum diameter of work-roll depends on the width of the roll face, that is, on the width of metal rolled; usually the maximum ratio $\frac{\text{roll-face width}}{\text{work-roll dia.}}$ for brass-rolling mills is $2-3\frac{1}{2}$, so that in the case of rolling 26 in. wide strip the practical minimum roll diameter is about 12 in. The minimum work-roll diameter is also determined by the torque which can be transmitted by the pinions, which have a pitch-line diameter approximately that of the driven rolls, with the maximum practicable width of tooth. This last condition means that for heavy reductions on thicker metal the work-roll diameter may not be less than one-third of the roll face; but for maximum reductions per pass on thinner metal, where the necessary torque will be less, the minimum roll diameter consistent with lateral stiffness can be adopted. As already mentioned (p. 514), a recent development is to drive the support rolls, which will be large enough to carry the necessary torque, and these drive by friction the work rolls, which may be of the minimum diameter.

The old cluster or six-roll mill might be considered as providing lateral support of small work-rolls, but this design has the defect that the four backing rolls cannot be larger than about twice the work-roll diameter, and consequently the roll load which can be imposed is seriously limited. To overcome this limitation, the 12- and 20-roll "Rohn" mill was developed; the former provided a second "layer" of support rolls over the two rolls which backed-up each of the work rolls in a cluster mill, and the 20-roll mill added a third layer. In each case the outer rolls carried the rolling load. This multiplication of rolls had the object of providing greater support for the work-rolls, or for a given roll load of allowing the use of even smaller work-rolls. These designs, unsuitable for high rolling speeds, have not been adopted in this country as production units for non-ferrous strip rolling.

The more recent development of the Sendzimir mill in its latest form follows from the 12- and 20-roll Rohn mills and is a very ingenious invention (see Fig. 4). It is, in effect, a 12- or 20-roll mill, but the outer

support is provided by lines of roller bearings, which are supported directly by the main-frame casting, with the further important difference that the mill work-rolls are driven only by friction from the supporting rolls, which are geared to the driving motor in the same way as in the case of four-high mills with driven support rolls. The Sendzimir mill is essentially a reversing mill with high coiling tension; the coiling power, which is generally approximately equal to the main mill motor power, assists in the actual work of deformation. With the proportionately very small work-rolls (ranging from $\frac{7}{16}$ to $2\frac{3}{8}$ in. dia., depending on the width) it is not possible to enter the strip into the

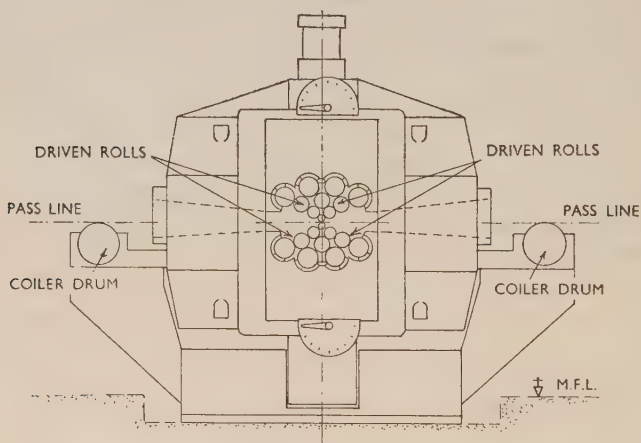


FIG. 4.—Arrangement of Sendzimir Mill.

rolls already adjusted for the reduction required, and the metal must be threaded through to the coiler with the roll gap opened and the pressure applied on the strip between the rolls. Considerable success is reported with these mills, especially on hard alloys and where thin and relatively wide metal is required. Several mills have been installed for soft metals, including copper alloys, where the basic advantage of the small work-roll diameter (and consequently small contact area for any given reduction) makes it possible to continue rolling on heavily work-hardened metal, and to obtain the maximum possible total reduction in thickness between anneals.

Sendzimir mills rolling softer metals are specified to run at high rolling speeds, the dissipation of the considerable amount of heat generated being effected by the circulation around the rolls and supporting bearings of a large volume of cooled and filtered oil. These

mills are essentially precision machines requiring a very high standard of workmanship. There is the secondary advantage that the overall dimensions of a Sendzimir mill of any given capacity are small. It will be of considerable interest to see whether these mills compare favourably from the point of view of production costs with the more orthodox backed-up roll mills.

5. *Coilers.*

In all modern strip mills the coiler, whether of the drum or roll type, is a most important component. The provision of adequate strip tension to control the metal passing through the rolls, to ensure flatness and edgewise straightness, is very essential, and with increasing rolling speeds and heavier coils accurate regulation of tension to suit the strip section being rolled and automatic control of tension during the build-up of the coil on a reel or drum, are necessary.

For moderate speeds and coil weights, with small coil build-up, the modern version of the clutch-driven coiler has the merit of simplicity and low cost; but with higher speeds and heavy coils where the heat generated in a slipping clutch may become excessive and with the considerable change in torque during the winding of large-diameter coils the separate motor-driven coiler, with automatic electrical control of coiling tension during build-up, is generally adopted as an essential feature of a modern strip mill. In the case of a reversing mill the motors geared to the reels act alternately as power units and drag generators, the latter applying predetermined and automatically controlled back-tension.

Excepting with mills designed to take a limited range of reduction in standardized width and gauge, coiling tensions must be capable of a wide range of regulation and give stable coiling-tension on both maximum and minimum conditions at all rolling speeds, under steady running conditions, and also during acceleration and deceleration. This is a problem for the designers of electrical equipment for rolling mills, and it is generally preferable to keep the tension range as small as possible. Minimum tensions $\frac{1}{5}$ – $\frac{1}{8}$ of the maximum are normally provided. For wider ranges two motors, of equal or different powers, may be coupled together so that both can be used for high tensions and one only for the lower range. Generally it is necessary to compromise and limit the tension per sq. in. of strip section on the maximum thickness handled in a mill to the minimum required to give "flat" strip, in order to obtain the minimum tension necessary when coiling the thinnest metal handled by the mill. Fortunately, heavy specific tensions are not wanted when rolling thicker metal—which is not so sensitive to any variation in elongation across the width of the strip,

due to camber or temperature changes in the rolls—as with thinner strip, where minute changes in roll pressure across the roll face, due to the above-mentioned conditions, may cause considerable inequality in the elongation at different points across the width of the strip.

There is little advantage, if any, in increasing coiling tensions for any given strip cross-section above that necessary to maintain a good “shape” in the rolled strip, and in cases where excessively heavy tensions appear to be required this is generally due to incorrect roll camber and roll temperature control. For brass-strip rolling, coiling-tension of about 6000 lb./in.² of strip section is in accordance with average practice.

The roll-type coiler, usually of the up-coiling type, is standard equipment for mills dealing with thick metal which is coiled for convenience in handling. It is quite automatic in action, the strip passing direct from the rolls and being engaged by the coiler rolls without stopping or slowing down the mill. It consists of three bending or coiling rolls, and two coil-carrying rolls; these latter keep the coil rotating as it is formed in the nest. All rolls are driven, and the coiler may be driven by gearing from the mill, or by a separate motor synchronized with the mill speed. Roll coilers handling heavy gauges have, in addition, a pair of feed or pinch rolls which ensure entry of the end of the strip into the bending rolls.

A pneumatically-operated ejector is provided to discharge the finished coil, which may be rolled down a ramp on to a coil conveyor. Where a “tail” or straight end is required for re-entry into mill rolls for subsequent passes, a “tailing” device is geared to the ejector, and the upper bending roll is raised, thereby allowing the tail end of the coil to pass through the coiler rolls without being bent. The length of tail is regulated by timing the action of the ejector-operating valve, or it can be automatically controlled by a light cell.

Roll-type coilers are designed to deal with strip up to 0.4 in. thick, and in smaller sizes down to a minimum of about 0.04 in. This type of coiler is designed to take any normal width of strip. Such a coiler is shown in operation with a four-high mill in Fig. 8 (Plate LIII).

6. *Rolling Speeds.*

It is now many years since cold-rolling speeds for non-ferrous metals were rarely greater than 100 ft./min., and it was about 20 years ago that it was proved that with efficient roll bearings and modern mill design speeds of 250 and 300 ft./min. were not only practicable but economical. The most economical rolling speed depends fundamentally

on the weight, and consequently the length, of coil available, and with brass ingots weighing about 100 lb. speeds of 150–300 ft./min. were probably sufficiently high; but with increasing coil weight speeds have been raised until now in the United States brass strip in one plant is rolled at 2000 ft./min. In this country few high-speed mills have as yet been installed, and wider strip mills built during recent years for this country and Europe have generally been designed for, and operated at, speeds up to 400 ft./min. But it seems certain that any new modern brass-strip mill, where coil weights from 600 to 1000 lb. and heavier are available, will have a normal speed range of 500–1000 ft./min. With increasing speeds it is necessary and economical to employ variable rolling speeds, preferably with Ward–Leonard control, so that not only can the strip be entered into the mill rolls and on to the coiler at a moderate speed, but the rolling speed can be regulated to suit the thickness and reductions taken. A constant motor horse-power range, from about half to full speed is also usually provided, so that maximum torque is exerted at the lower speed, at which any specially heavy reductions on maximum thickness of metal can be taken. This makes it possible to keep the motor running nearer its full load for all passes, i.e. at its maximum efficiency. It is sound practice when specifying the speed conditions for any new mill to fix the maximum at a somewhat higher speed than that which is considered suitable for the requirements at the time, thereby providing a margin for increasing speeds to the maximum which may be found to be practicable and economical later on.

7. Motor Power.

The production obtainable from any mill may easily be unnecessarily limited by providing driving power less than it could safely carry, and in planning a modern strip plant a carefully considered schedule of rolling passes with corresponding maximum rolling speeds should be prepared, so that the probable maximum power required from the motor can be determined.

8. Roll Cooling and Lubrication.

Bearing in mind that practically all the work expended in rolling metal is converted into heat, it is easy to see that with more powerful mills, taking maximum reductions per pass at high speeds, a great deal of heat is generated, of which a considerable proportion is conveyed to the rolls, so raising their temperature. With the older slow-speed mills, even when taking very heavy reductions, the rate of radiation of heat from the roll surfaces was sufficient to balance the rate of heat input without special means of cooling other than the circulation of

water through the centre of the rolls. This method of cooling becomes entirely inadequate in the case of the modern high-speed mill, and external cooling of the rolls by sprays must be provided. It will also be obvious that with the increasing use of the backed-up roll mill, with work-rolls of smaller diameter in relation to strip width and power input than with the larger roll diameter of the two-high mill, higher roll temperatures and more rapid changes in roll temperature will result.

There is no objection to a high roll temperature in itself, but excessive fluctuation in temperature, especially wide variations in temperature across the face of the rolls, causing changes in roll shape and resulting in variations in gauge and bad shape of strip, must be avoided. With external cooling of the rolls, the cooling media must be selected to serve also as a suitable lubricant. The lubricant applied to the strip in the old-type slow mills was usually a mixture of water and oil, the coil being immersed in a bath containing water with a film of oil on its surface through which the strip was drawn into the rolls, or the lubricant was "swabbed" on to the strip in a more or less haphazard manner. The general practice in America is to use water combined with oil as a rolling lubricant, and this is a very efficient cooling medium. For some light-gauge strip finishing a heavier lubricant will increase the reducing power of the rolls, and a suitable mineral oil may be required; although this is not such a good cooling medium as is a liquid containing a large proportion of water, it can be adequate to maintain stable roll-temperature conditions and uniform roll shape. Soluble oil may also be used, and is efficient both as a lubricant and coolant.

9. Gauge Control.

Accurate control of gauge in all cold-rolling mills is of supreme importance, and with ever-increasing speeds, combined with the heaviest possible reductions per pass, this becomes more difficult to attain. The fitting of automatic gauging instruments or flying micrometers is now standard practice; these gauges continuously measure the thickness of the strip leaving the rolls, and an indicator shows immediately the least divergence plus or minus, from the pre-set gauge desired. This indication enables the operator to increase or decrease the roll pressure (or alternatively to vary the rolling speed) and thereby hold the gauge constant throughout the length of the coil within fine limits.

Some attempts have been made to make the roll adjustment for gauge correction automatic, but so far no very practical automatic equipment has been evolved.

Recently the question of designing a pre-loaded four-high mill has

received some attention, and although many practical difficulties arise, these will eventually be overcome. If the roll gap can be set under a pre-load which is in excess of the maximum roll pressure required for any pass reduction, this should be an ideal method of maintaining a uniform strip thickness.

Apart from possible future developments on the lines suggested above, for accuracy and uniformity of finished gauge, it is important to maintain gauge control from the start to finish of cold rolling beginning with the earliest breaking-down passes.

III.—ROLLING OF ALUMINIUM AND ITS LIGHT ALLOYS.

1. Sheet and Strip Rolling.

In considering the cold rolling of aluminium and its light alloys, it is necessary to bear in mind that there are three main groups of these metals :

(a) Strong alloys, as used for aircraft construction, whose physical properties are obtained by final heat-treatment and not by cold working.

(b) Medium-strength alloys containing 2-5% magnesium, which work-harden very rapidly, and therefore require a relatively small degree of cold rolling to acquire the desired properties.

(c) Aluminium itself, in varying degrees of purity, and lower-strength alloys, particularly the 1½% manganese alloy, which must be subjected to an appreciable amount of cold working to comply with relevant specifications.

Alloys in groups (a) and (b) are more readily reduced by hot rolling than cold rolling; with group (b) several intermediate anneals are required to maintain a condition which is rollable. The pure metal and soft alloys in group (c) can be easily cold rolled, and will stand a considerable amount of reduction before annealing is necessary. The different properties of these three groups of light alloys have a considerable influence on the type of plant installed.

It must also be remembered that for all groups a certain amount of cold reduction is necessary from the point of view of surface finish, flatness, and accuracy to gauge; certain metallurgical considerations also require some cold working of the metal, even before the temper-anneal point.

While considerable progress in the technique of cold rolling aluminium and its alloys has been made during the last 20 years or so, this progress continued with greater rapidity during the last war and the recent post-war years. Previously only relatively light ingots of about 250 lb., 3 or 4 in. thick, were available, and such small slabs were

hot rolled in simple non-reversing pass-over two-high mills to $\frac{3}{8}$ or $\frac{1}{4}$ in. thickness, in widths of 12–18 in. Cold rolling of thin strip was generally effected in slow-speed two-high mills with rolls 12×20 , 14×24 , or 16×30 in. for finished strip production. Such strip mills were of the Continental slow-speed type and, with the relatively long roll barrels as compared with the diameter, economical reductions could be made only with heavy roll camber. For wide sheets, the hot-rolled narrow strip was sheared to lengths corresponding to the width of sheet, and these were cross-rolled in two-high sheet mills, with rolls usually varying in diameter from 24 to 28 in. and having face widths from 60 to 80 in., in an exactly similar way to the old method of cold rolling brass and copper sheets described in Section II.

Even with heavily cambered rolls, a great number of passes were required to reduce sheet blanks $\frac{3}{8}$ in. thick to sheet gauges. In the decade 1925–35 the practice in both sheet and strip rolling was changed greatly by the influence of American practice, particularly in regard to strip rolling, for with the demand for increased production in wider strip, the old-type strip mills became uneconomical. For pure aluminium strip required for aluminium foil production, hot-rolled slabs of limited weight, about $\frac{5}{16}$ in. thick, were cold rolled in reversible two-high mills with rolls about 18×36 in., following Continental practice, and consequently at low speeds around 80–100 ft./min. As in the case of brass-strip rolling with improved mill design, particularly in regard to more efficient roll bearings, this size and type of mill was successfully operated at higher speeds of 150 ft./min., and where only light ingots are available similar mills have been installed in recent years.

The example of American practice resulted in the building and installation in this country of much more powerful two-high strip mills having rolls of much greater diameter and of much heavier design. This marked a complete departure from Continental practice, and mills were installed with rolls 20 in. dia. \times 40 in. face and larger. These mills were generally non-reversing and were capable of cold roughing from hot-rolled strip about $\frac{1}{4}$ in. thick in widths of 24–36 in., and final finishing.

Generally, the roughing mill of this type was operated at a constant speed of about 150 ft./min., powered with a motor of 150 h.p., while similar mills with the same roll dimensions were used to finish the strip, reduced in the roughing mill to about $\frac{1}{16}$ in. thick or less, to the required final gauge. These finishing mills were driven by variable-speed motors of 300–350 h.p., giving rolling speeds of 150–300 ft./min. Two-high mills of this type are still economical production units where moderate coil weights are handled. With the installation of two-high

reversing hot mills capable of rolling heavier and thicker ingots in all types of light metal, heavier coils became available to the cold mills. With the development of these more efficient two-high strip mills, the accessory equipment such as bridles, coilers, &c., was also greatly improved.

With the roughing mill of this type, roller bridles, pneumatically

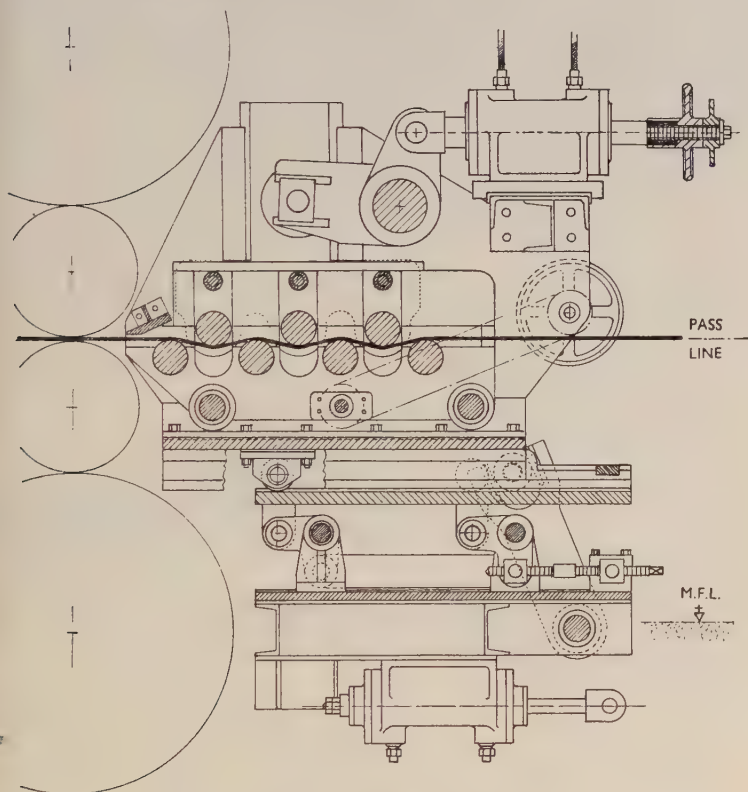


FIG. 5.—Combined Bridle and Feed-In Device.

or hydraulically operated, were fitted to control the strip at entry to the rolls, providing a degree of back-tension. Fig. 5 shows a modern type of roller bridle, with adjustable side guides. As mentioned earlier in dealing with the rolling of copper and brass strip (p. 516), the roller bridle is as yet used only in light-alloy strip rolling.

The roughing mill, from which strip about 0.1 in. thick is delivered, is also fitted with a roll-type coiler, as described in Section II (p. 514),

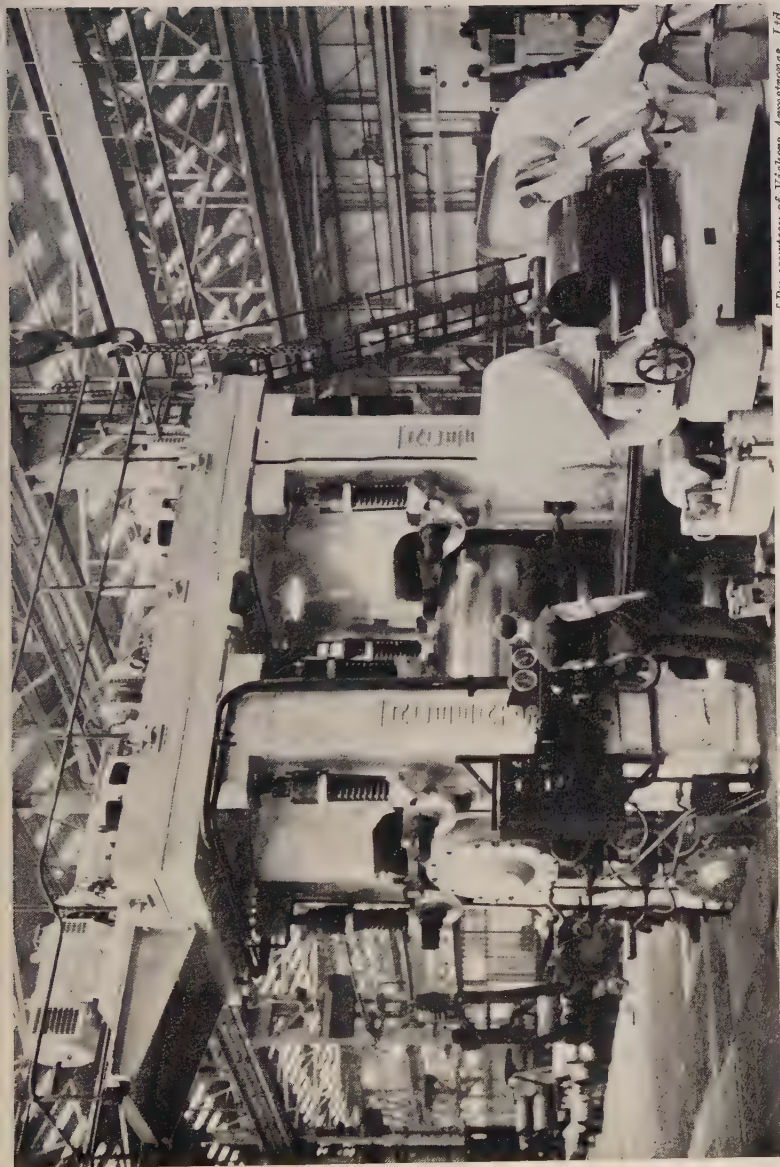
with automatic coil ejector and a "tail-pulling" mechanism. As the roll coiler can operate effectively only on relatively thick metal, the finishing mill starting with strip at 0.1 in. is provided with a drum coiler, which is fitted with a pneumatically- or hydraulically-operated coil ejector. This can also be made to take strip automatically, without stopping the mill, by means of a belt wrapper; this last is especially advantageous when finishing to light gauges. Two-high finishing mills were, and still are, installed as reversing units with friction clutch and brake-controlled drum-coilers on both sides of the mill.

An example of the latest development in two-high strip mills is the 30 × 60 in. reversing mill capable of handling heavy coils in widths up to 50 in. or so. Fig. 10 (Plate LV) shows one of two reversing two-high mills at the Falkirk Works of The British Aluminium Co., Ltd., with rolls 30 × 60 in. These mills are especially suitable for finishing and temper-rolling pure aluminium and soft alloy strip up to 48 in. finished width. The mills are driven by variable-speed motors of 600 h.p., giving rolling speeds up to 360 ft./min. Drum-coilers with automatic tension control are installed on both sides, driven by motors of 225 h.p. This illustration is selected to show the equipment at the entry side, which consists of a cone-type decoiler, provided with hand-operated brakes, the cones being carried on adjustable sliding heads, which can be moved laterally to receive the coils and for adjustment to suit the width of coil.

Up to 1938 the four-high mill had not been favoured in this country or on the Continent for rolling either aluminium sheet or strip, as it was thought that with soft metals such as pure aluminium and the softer alloys the rigidity and power of the backed-up roll mill was not necessary; but with the development of the strong and hard alloys for wide strip and sheet the four-high mill inevitably came to the fore. Experiments on four-high mills built for other metals proved their greater capacity for heavy reductions, and consequently for increased productive efficiency, and led to the installation of this type of mill for all types of light alloys.

In the first instance these mills were employed for wide sheet rolling, and several powerful mills were supplied just before and during the last war; the advantages in reducing the number of passes and the greater uniformity of gauge achieved across the width of the sheet were, as in the case of copper and brass sheets, definitely proved.

The practice in sheet rolling in four-high mills was much the same as for other non-ferrous metals, but with the increasing weight of ingot and the hot rolling of wide strip delivered to the cold mills in coils, wide-strip rolling was adopted in this country for the earlier roughing passes.



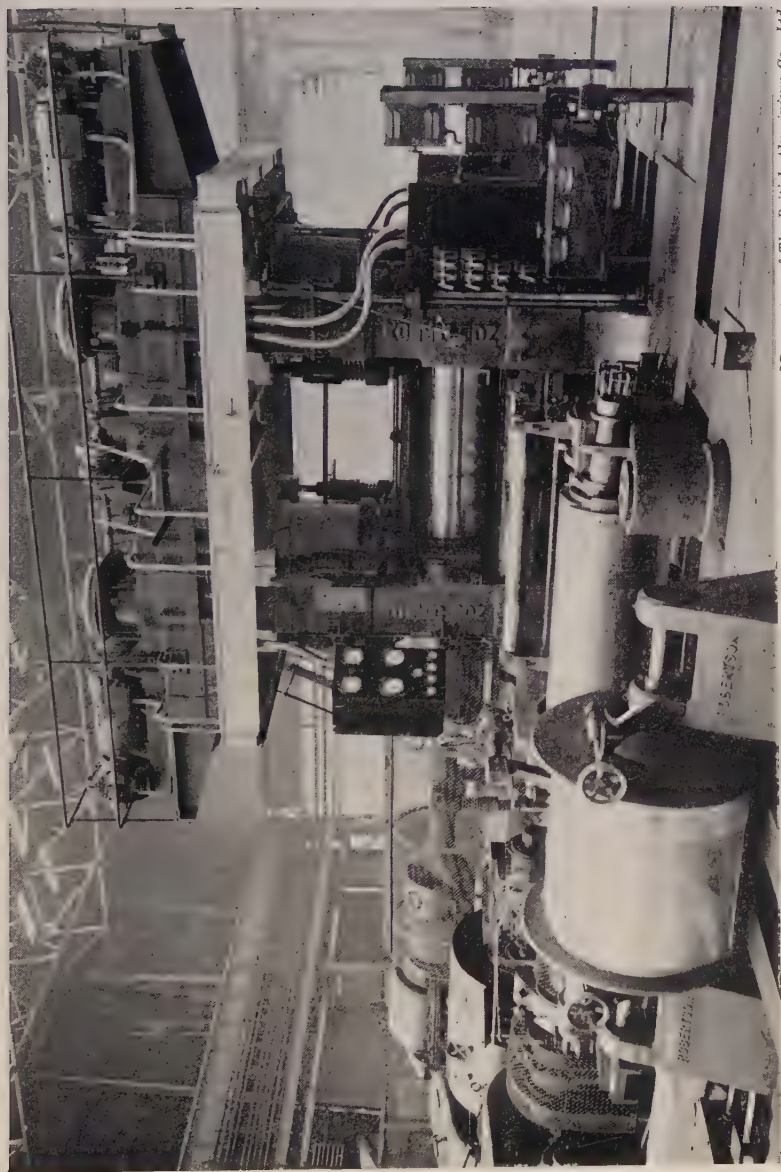
[By courtesy of Vickers-Armstrongs, Ltd.]

FIG. 8.—A 15 × 37 × 60 in. Four-High Non-Reversing Brass-Strip Mill.



[By courtesy of The Enfield Rolling Mills, Ltd.]

FIG. 9.—A 12 × 30 × 34 in. Four-High Reversing Brass-Strip Mill.



[By courtesy of The British Aluminium Co., Ltd.]

FIG. 10.—A 30 · 60 in. Two-High Reversing Strip Mill for Wide Aluminium and Light Alloy Strip.

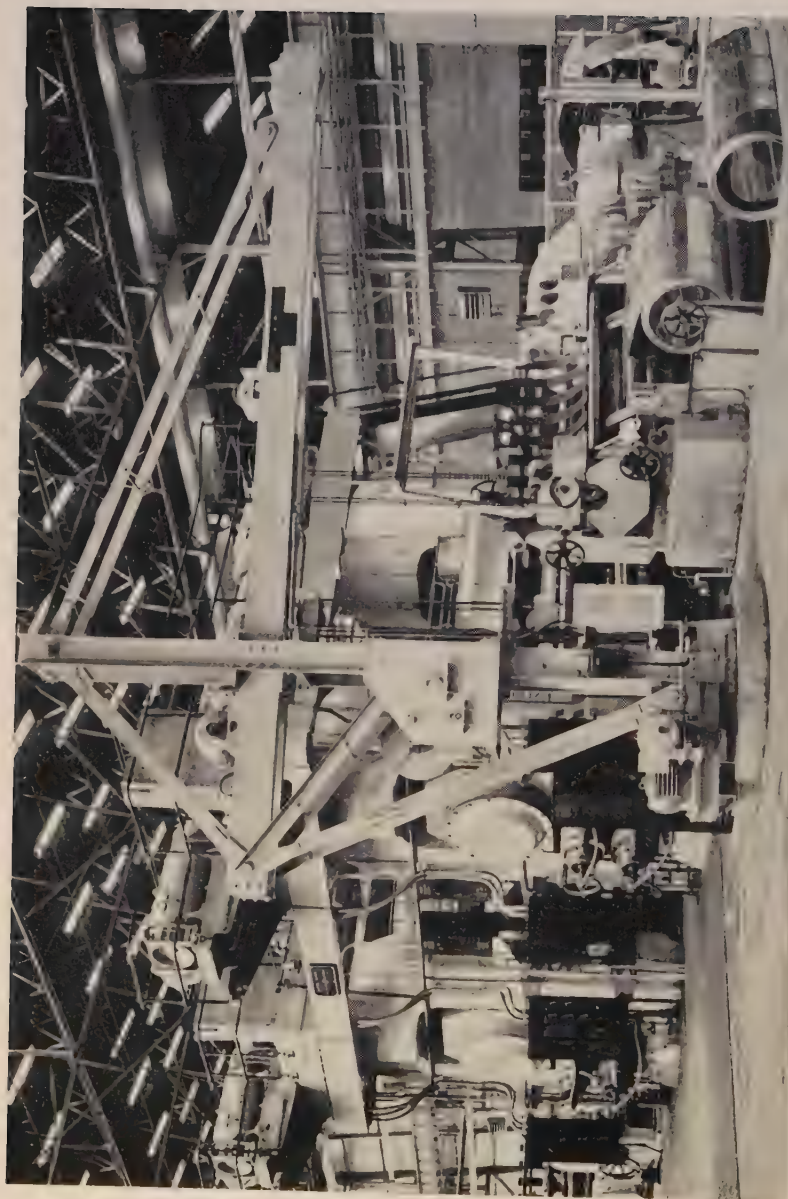


FIG. 11.—A 20 × 49 × 84 in. Four-High Two-Stand Tandem Cold-Rolling Mill for Wide Aluminium and Light Alloy Strip.
[By courtesy of The British Aluminium Co., Ltd.]

That is to say the hot-rolled strip was reduced to a gauge suitable for finishing to sheets in non-reversing four-high strip mills, with automatic roll-type coilers and roller bridles. Coils received from such mills were flattened and cut to suitable lengths, and finished as before in four-high or two-high sheet mills.

Further developments in wide-strip rolling took place very quickly, and in 1941 the first tandem continuous wide-strip mill in this country for aluminium, was built by W. H. A. Robertson and Co., Ltd., and installed in the Rogerstone works of the Northern Aluminium Co., Ltd. With this, strip up to 52 in. wide was most efficiently reduced in one pass through three stands of rolls continuously to the required finish gauges, suitable for flattening and shearing to sheet lengths. Developments on these lines had already taken place in the U.S.A., and for mass production of wide strip the four-high tandem cold strip mill was firmly established.

Fig. 11 (Plate LVI) shows a two-stand four-high tandem mill in the Falkirk Works of The British Aluminium Co., Ltd., capable of rolling strip up to about 72 in. wide. The work-rolls are 20 in. dia., with support rolls 49 in. in dia. by 84 in. in face width. Each stand is driven by a D.C. variable-speed motor of 1500 h.p., giving rolling speeds of 0-450 ft./min. Roll-type up-coilers are provided at both ends of the train, which can be operated as a reversible unit when rolling thick metal, the up-coilers being equipped with an additional flattening roll for use when entering the strip into the rolls, and acting as a decoiling and feed unit. For finishing, a drum-coiler is placed at the normal outlet end, driven by a variable-speed D.C. motor of 550 h.p. with automatic control to maintain constant tension during the build-up of the coil. Pneumatically-operated roller bridles are fitted on both stands, as required when the train is working as a reversible unit. Fig. 11 shows a coil entering from the coil box. Electrically-operated jib cranes are installed for lifting the coils after ejection from the coiler, and placing them on power-driven trucks for floor transport.

It should be noted that the mills illustrated in Figs. 10 and 11 (Plates LV and LVI) were designed and installed during the last war, primarily for the production of sheets for aeroplane construction.

A question arises as to whether such a tandem train should consist of two or three stands; the answer to this depends on the total reduction which can be effected before annealing is necessary, and for most alloys a two-stand mill would appear to be capable of effecting the maximum reduction necessary. In the case of thin strip, of the order of 0.010 in. thick, required in pure aluminium or soft alloys—where the total reduction before anneal can be considerable—a three-stand mill

is economically employed. It may be noted here that at the Isoire plant in France ² a two-stand cold train is installed.

As indicated above, the number of stands provided in any tandem train depends largely on the degree of cold rolling which can be economically effected on the particular alloy to be handled. The approximate total percentage reduction which can be taken on the three main groups of light alloys are :

Strong alloys, group (a) 50%.

Magnesium-containing alloys, group (b) 30%.

Pure aluminium and soft alloys, group (c) up to 90%.

Reference to the description of a large French plant ² will show a further development in light-metal strip rolling, namely, the extension of hot rolling to much lighter gauges. The rolling from heavy ingots is carried out in stages, usually at one heat, by means of one or more two-high or four-high reversing mills followed by a two- or three-stand four-high continuous train, which delivers strip, still warm, in thicknesses which require only a small total percentage cold reduction to finish to final gauge. This development in hot-rolling practice will have considerable influence on the type of plant required for cold finishing. Cold roughing, which was necessary when the hot-rolled strip was supplied in thicknesses ranging from 0.4 to 0.2 in. is eliminated, and the intermediate anneal is avoided. With the latest practice, strip may be reduced in the hot mill train to gauges down to 0.100 in. thick, and possibly less. This strip must be sufficiently cooled before coiling, and the last reduction may be taken at a relatively low temperature. This stage may be described as "warm" rolling, and the tendency is to merge the hot and cold rolling of a considerable range of light alloys into one continuous process. In America, where the outputs required are very large, the hot train may comprise a multiplicity of stands, the product of which is passed to a cold tandem train of three or more stands.

With the possibility of hot finishing or "warm" rolling to a thickness closer to the finished gauge, the number of stands required in a tandem train might be reduced to two, and for some classes of product a single-stand mill would be sufficient to give the desired surface finish and accuracy. This may be a reversing mill when two or more passes are needed, but, as in the case of copper and brass strip rolling, there is much to be said for the one-way mill, with mechanical-handling equipment for batch-rolling.

An example of the combination of reversing and non-reversing cold plant is an installation of two four-high mills, one for roughing and

one for finishing; the former takes hot-rolled strip at about 0.350 in. thick which is transferred to the cold-roughing four-high mill by vacuum-suction lift and transporter. The earlier passes are taken on the flat, reversibly, the final pass being coiled in an up-coiler. This mill, which has rolls 16 in. and 37×60 in., is driven by a motor of 1000 h.p.

The coils from this mill are conveyed to a finishing mill of similar size which is non-reversing, running at 625 ft./min. and also driven by a 1000-h.p. motor. Two or more passes may be taken and the coils are conveyed from one side of the mill to the other by a roller conveyor; an up-ending device is provided at both entry and exit sides. A drum-coiler and belt-wrapper are provided, and at the entry an unwinder and "tail-pulling" equipment. The coils come to the mill stacked on end on a conveyor, are turned through 90° , and delivered on to the mill approach rollers; the "tail" is drawn out by an equipment consisting of feed or pinch rolls and flattening rolls. An up-cut shear is installed so that the scrap ends may be cut off. The pinch rolls are reversed and the coil is ready for rolling; it is then carried forward to a cone-type decoiler and the long tail entered into a roller bridle fitted to the mill, and thence through the mill rolls and to the coiler with belt wrapper. On completion of the pass the coil is ejected, turned 90° on to its end, and transported back on the roller conveyor to the feed side of the mill, where the operation may be repeated.

A suitable number of coils can be stored on the conveyor to form a convenient batch. This finishing mill, with its mechanical coil handling, may be cited as typical of a modern non-reversing mill, and has a high production efficiency.

Correct proportions of the rolls for four-high cold strip mills are important. The support-roll diameter will be decided by the maximum rolling load to be carried and the necessary dimensions of the roll bearings, whether of the roller or film-lubricated, plain-journal type. But the diameter of the working rolls may vary within fairly wide limits and the ratio of diameter to face width can be as much as 4 : 1. At the same time the diameter should logically be as small as possible, consistent with the strength necessary to withstand the maximum driving torque. The question of temperature control and the maintenance of correct roll shape must also be considered. With present high rolling speeds, external cooling in addition to lubrication must be provided with means for controlling distribution. Generally, coolant containing water is not suitable for aluminium rolling, and the problem of obtaining a medium which will lubricate and cool efficiently without causing staining of the metal surface is, as pointed out in the paper by Thomas and Fowler,³ difficult to solve. Special oils have been developed

and are used with satisfactory results, and where a considerable amount of heat is generated a copious external application of cooled and filtered oil is necessary.

The quantity of coolant required for efficient temperature control of the rolls will naturally depend on the liquid employed, and as the heat generated in the roll gap is approximately proportional to the power applied to the rolls, it can reasonably be based on the mill motor power.

The progress with warm rolling to gauges nearer to the finished cold-rolled thickness may help towards the solution of the roll-lubricating and cooling problem, in that it is possible to use a solution of soluble oil in water in the four-high hot-finishing train, provided the leaving temperature of the strip is high enough to evaporate the solution. Oil must, however, be used in the cold-finishing mills.

Rolling speeds have increased considerably, and a modern cold strip mill of the type described above would now normally be designed for a maximum speed of about 1500 ft./min. The three-stand tandem cold mill in the new continuous strip plant of the Northern Aluminium Co., Ltd., at Rogerstone is designed for a maximum speed of 2000 ft./min.

Recent experience indicates that aluminium and its alloys roll more easily and require less power per ton at high speeds than at low, presumably owing to the higher temperature of the rolls and metal. As with other metals, the maximum economical speed must depend on the size and consequently the weight of coil available, but with the increase of ingot weight to 2000 lb. and heavier, high speeds are definitely economical.

Very light-gauge strip in narrower widths, slit from standard, wide, hot-rolled stocks can probably best be finished in a multi-stand tandem mill, and the maximum delivery speed from such a train should be as high as is required for the desired output. One of the difficulties with high-speed rolling is due to the need for starting and threading at a slow speed, and the consequent change in gauge due to acceleration and deceleration, in addition to the effect of roll-temperature changes. Gauge control is another problem which is not yet completely solved.

The flying micrometer is an essential equipment for any modern strip mill, and enables the operator to adjust the roll setting as necessary to maintain a uniform gauge (see p. 522).

2. Auxiliary Equipment.

Correctly designed coiling equipment—essential with any modern cold strip mill—and automatic tension control by one or other of the well-known electrical systems is universally adopted.

Coiling drums must have mechanically or hydraulically operated collapse and efficient coil ejectors, usually hydraulically operated, and a coil carriage having hydraulic lift to deal with varying coil diameters is provided. The coiling of cold-rolled light-metal strip where a high standard of finish is required is another problem owing to the ease with which aluminium and its alloys can be scratched and marked.

Collapsible drums in which the segments forming the drum surface leave spaces between them when the drum is fully expanded are objectionable, especially for thin metal, as the radial compression of the

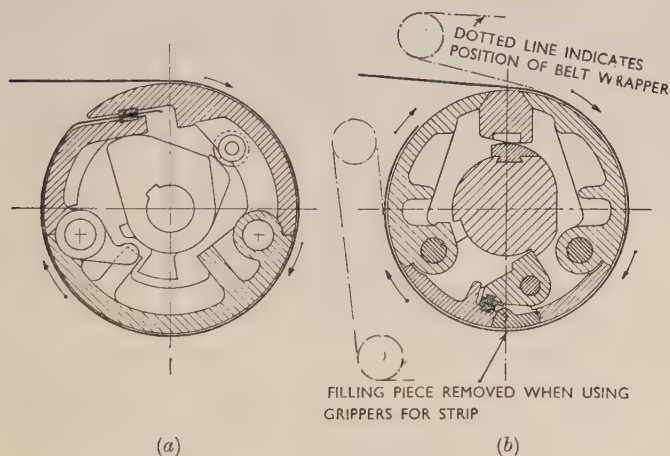


FIG. 6.—(a) Hinged-Type (b) Wedge-Type Collapsible Drum.

outer layers of the coil, due to the tension applied, causes the inner layers to bulge into the gaps, leading to marking that may persist even after further reduction. The design with two hinged segments (Fig. 6 (a)) which are expanded by cams on taking up the tension has been much used and is satisfactory for heavier gauges, but as this has a gap into which the end of the strip is inserted and gripped, there is the same risk of marking at this point. This defect is eliminated by the use of the belt wrapper which automatically wraps the strip round the drum, holding it until sufficient layers are wound to give the necessary grip to withstand the tension, after which the wrapper can be withdrawn. This equipment, besides rendering unnecessary any slot for gripping, avoids stopping or slowing down to enter the end of strip into a gripping slot. With this device the collapsible drum itself should present a

smooth, unbroken, cylindrical surface, and the wedge-type drum (Fig. 6 (b)) is designed to meet these conditions.

For very thin metal, it is often necessary, or preferable, to use sleeves, which can be placed over the drum itself and used with the belt wrapper; the finished coil is ejected on the sleeve, and may either be removed from the coil by a separate re-winding process under light tension on to a collapsible drum where the coils can be passed directly to another process such as slitting, or the re-winding can be done after this process and a separate re-coiling operation avoided.

An efficient ejecting device must be provided to strip the heavy coils from any coiling drum; this is either pneumatically or hydraulically operated, and may be combined with a coil-carrying wagon with hydraulic lift. This again may be provided with a tilting device so that the coil after being delivered clear of the drum can be tipped on to a conveyor and either returned to the inlet side of the mill, in the case of batch-rolling, or transported to any succeeding process line.

3. Mechanical Handling of Coils.

In any modern mill efficient and labour-saving methods of transporting and handling coils to and from the mills, furnaces, and process lines have become of primary importance, especially with the heavy coils now available, and the most efficient type and lay-out of suitable conveyors require careful attention and study.

Before considering systems for transporting coils, the means of handling the coils at the entry end of the mill and of inserting the strip between the mill rolls requires study. It is generally agreed that with heavy coils it is easier to get coils away from the mill after rolling than to enter the metal into the rolls. The hot-rolled coils may be tightly wound or delivered with a short "tail". In the former case, if the strip is thick a coil-opening machine is required, and in either case a "tail" pulling and flattening unit is necessary in order to get a reasonably straight tail of sufficient length to reach from the coil box or other decoiling device to the mill rolls. The coil-box type of decoiler may be suitable for heavy-gauge strip, but generally the cone type or expanding mandrel type of decoiler is to be preferred; such a decoiler is shown with the 30 × 60 in. reversing two-high mill (Fig. 10, Plate LV). The cone heads are adjustable by electric motor, and mechanically-operated brakes are fitted to provide a light back-tension. In some decoilers of this type a drag generator is geared to the cones to give them this back-tension, and these generators can be operated as motors to turn the cones and feed the strip forward into the mill.

A recent improvement is the combined decoiler and bridle fitted at the entry side of the Davy-United three-stand tandem cold strip mill at the Rogerstone Works of the Northern Aluminium Co., Ltd. This equipment consists of a cone-type decoiler with a pair of adjustable-diameter cones, which are carried on brackets having means of adjustment to suit varying widths of coil, with a seven-roll bridle (similar to that illustrated by Fig. 10, Plate LV). This combined uncoiler and bridle unit is mounted on slide beds, on which it is traversed by hydraulic mechanism towards the mill rolls to give a "sticking" action. A travelling coil-loading jack is also provided, with a traverse stroke sufficient to feed the "tail" of the coil through the open bridle.

The sequence of operation to feed the coil into the mill is as follows :

1. The coil is discharged from the slat conveyor on to the coil jack.
2. The elevator lifts the coil to the correct predetermined height.
3. With the combined uncoiler and bridle at the beginning of the sticking stroke, and with the cone and bridle open, the coil is traversed into the mill, the tail of the coil being simultaneously fed through the bridle daylight.
4. The cones are closed into the coil.
5. The elevator is lowered.
6. The bridle is clamped to the predetermined penetration.
7. The sticker is actuated and the tail end of the coil is fed into the mill work roll bite, and the lift is traversed outwards to its original position to receive the next coil from the conveyor.

For transportation of coils to and from the mill and other process lines coils may be up-ended and transported on their ends, or carried with their axes horizontal; the choice between these two alternatives must depend on individual conditions. Soft coils, if transported horizontally, may collapse by their own weight and lose their circular form. On the other hand, if carried on their ends by roller tracks the edges may be burred and damaged.

Generally, transportation with the coil axis horizontal is favoured, and where coils are wound and transported on sleeves, deformation due to weight is prevented. For the mechanical handling of coils to and from a mill or other process plant there is the choice of many types of transporter—Vee-type roller tracks, which may incline to utilize the force of gravity to move the coils along, idle- and live-roller transporter tracks, belt and "slat" conveyors—all of which have their advantages in particular cases. Vee-type roller tracks are most useful where coils are to be moved by gravity (or manually) in the direction of their

axes, whereas when it is more convenient to move the coils in a direction at right angles to their axes the slat conveyor is most suitable. Further, while an inclined Vee roller track can be provided with braking sections and buffers to slow down and arrest the motion, the mechanically-driven slat conveyor can be accurately controlled, providing either continuous or intermittent motion as required. Wooden slats shaped to minimize damage to coils can be placed so that each coil is uniformly spaced conveniently for removal and transportation by "fork" or "pole" trucks, or by overhead cranes with single or multiple lifting hooks.

A typical example of coil handling for a non-reversing wide-strip rolling mill is illustrated by Fig. 7; at the entry side of the mill an inclined Vee roller track (*A*) of sufficient length to accommodate a convenient number of coils provides for the feeding of each coil into the cone decoiler; a braking section and "flag" stop is placed to arrest movement and allow the leading coil to be deposited on a turntable. The coils are thereby turned through 90° and are rolled on to Vee rollers carried on the head of an hydraulic lifting ram, by means of which the coil is raised into alignment with the cones, which are then closed and the "tail" entered into the mill rolls.

At the outlet end the coils are supported by a Vee roller section on an hydraulic jack mounted on a slide, and are mechanically ejected from the coiler drum. The coil with the hydraulic jack is pushed clear of the drum and rolled on to a fixed Vee roller track to a turntable, which again turns the coil 90° and from which it is deposited on a return gravity Vee roller track (*B*) long enough to take a batch of coils; at the lower end of this another braking section and "flag" stop is provided.

Where a second pass is required, the coils can be transferred to track *A* by overhead crane or runway, or by "fork" tracks, and the sequence of operation repeated; or if the coils are finished they can be conveyed singly or in batches by the same overhead or floor transport to annealing furnaces, slitting and cut-up lines, &c.

The details of a system such as is described above can be varied to meet individual cases, and by suitable arrangement of controls the handling operation can be made largely automatic, so minimizing the labour required. Similar systems modified to suit the conditions can be provided to serve reversing single-stand or tandem trains.

An alternative coil-handling equipment for a one-way single mill is described on p. 519, but in that case the coils are up-ended and are transported by conveyors on their ends. For transporting sheets and flattened cut lengths of strip the belt conveyor is most conveniently adopted.

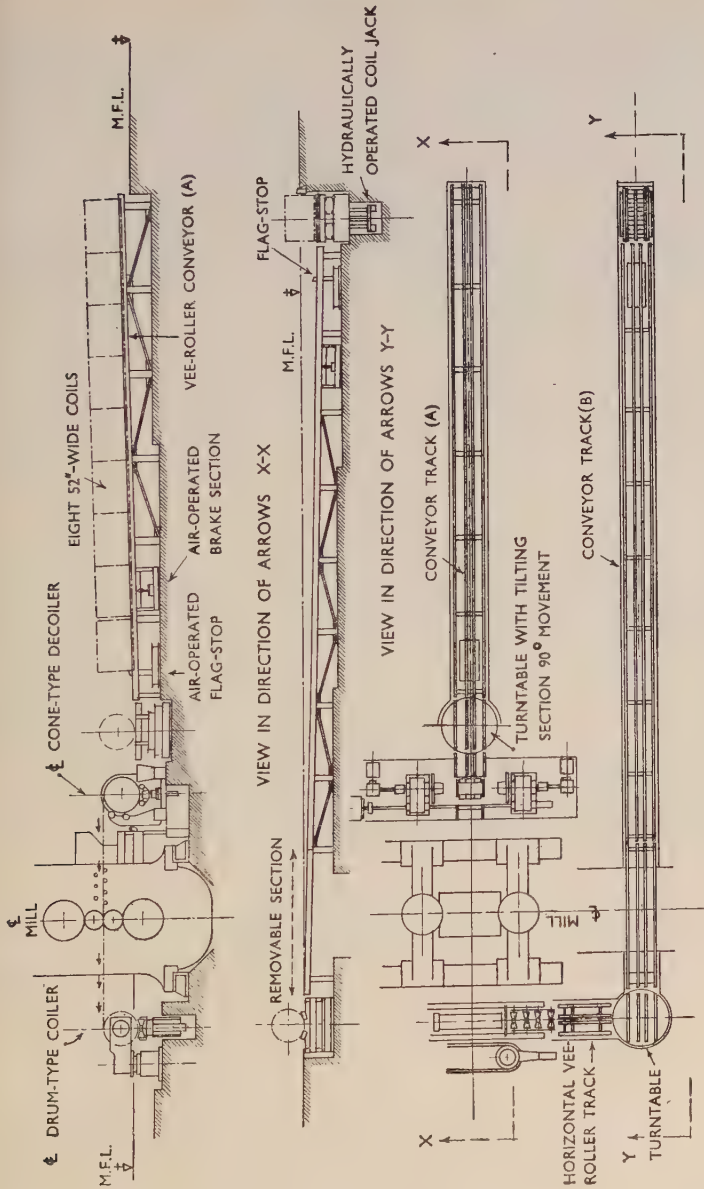


Fig. 7.—Arrangement of Coil-Handling Equipment for Non-Reversible Mill (Batch-Rolling).

4. Accessory Plant.

While not strictly a part of the rolling mill, accessory machines for such processes as edge-trimming, slitting to multiple widths, flattening and cutting to length for sheets, &c., form an important part of any cold-rolling mill whether handling copper alloys or light metals, and while space does not permit any account of such equipment in the present paper, there are many mechanical and metallurgical problems which deserve study in connection with plant for these accessory processes.

There is, however, one point which may be noted in regard to edge-trimming, particularly in the case of aluminium and light alloys; with many strip mills for both wide and narrow metal in the past the edge-trimming and scrap-cutting equipment has formed a part of the cold-rolling mill itself, the strip being trimmed to width between the mill rolls and coiler. It is now generally agreed that the mill proper should be as simple as is consistent with the efficient operation of its essential purpose, and that edge-trimming should be carried out in a separate line.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge the help and advice given to him in the preparation of this paper by many friends in the non-ferrous and light metal industries, and regrets that their number does not permit individual mention. He is particularly indebted to the firms who have kindly allowed the use, as illustrations, of photographs of mills installed in their works.

He would especially thank Mr. R. S. Storrs, Senior Vice-President of the Torrington Manufacturing Co., U.S.A., for his very complete reports on non-ferrous metal rolling practice in America.

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WIRE-DRAWING TECHNIQUE AND EQUIPMENT.*

1289

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SYNOPSIS.

The principal landmarks in the development of the wire-drawing industry in this country from the earliest beginnings until the present time are reviewed. A description is then given of present-day machines, comprising tandem- and cone-type machines, in which slipping of the wire occurs in the course of drawing, and also the non-slip variety. Die design, die materials, lubricants, speeds of drawing, reductions, and other aspects of wire drawing are dealt with, and a detailed account is given of current practice in the production of copper, brass, bronze, and other copper-alloy wires, and also of aluminium and alloy wires. Finally, various types of defects which are encountered are considered.

I.—HISTORICAL.

It is popularly believed that wire is a modern product and that its importance dates only from the evolution of electric power. In fact, wire making is one of the most ancient crafts, extending back for about five thousand years. As far as is known the earliest wire production was entirely in non-ferrous metals, and it is generally accepted that the manufacture of iron and steel wire was introduced into the craft only a few centuries ago.

1. *Early References.*

As a result of archæological studies, there is proof that the ancients were skilled in the production of gold, silver, copper, and bronze wires, which were used for ornamental purposes only. In some instances gold filaments were as small as 0.010 in. in dia. The earliest examples, assumed to have been made about 4600 B.C., were found in Syria, and it is probable that these were produced by hammering and not by drawing. However, there is proof that by the year 4000 B.C. the Egyptians had discovered how to draw wire with dies consisting of holes bored in hard wood. There is also evidence that by the same period the Chinese were using dies which consisted of tapered holes in stones.

Production on anything like a commercial scale was first undertaken in Europe about the fourteenth century, the industry being mainly developed in Germany and Westphalia, where the use of the

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† British Insulated Callender's Cables, Ltd., Prescott, Lancs.

water-wheel was later applied, thus giving the first mechanically produced metallurgical product.

The making of wire began in this country in the middle of the fifteenth century, the necessary knowledge being brought over from Germany. The industry was established at Tintern in Monmouthshire, but little progress was made for a very long period, and over several centuries methods of production and general customs did not change.

After remaining static for many years, the wire industry received a tremendous impetus from the succession of discoveries in the electrical field during the nineteenth century. While these discoveries gave rise to a large demand for copper wire, and thus formed the basis of the great non-ferrous wire industry of to-day, they in turn made possible the cheap commercial production of iron and steel wires, by providing the means of power application to wire-drawing machinery.

2. Practice at the Beginning of the Twentieth Century.

At the turn of the present century wire was still being drawn by the single-hole method, the practice being commonly known as bull-block drawing. The dies were made by punching in a steel plate a series of holes of a suitable range of sizes, the final contour of the holes being secured by master punches, which were prized possessions of the wire-drawers. Rows of single capstans, power-driven from a common backshaft, were employed for drawing single lengths of wire, and as each reduction was effected, the iron or steel plate die was replaced by a smaller one, until all the drafts to the finished wire size were completed.

It is apparent that this method was both long and costly. Each of the plates or dies had to be sized and set by the operator for each coil of wire drawn; this required a fairly high degree of skill, and in a limited field the wire-drawer had to be his own tool-maker. Many of these tools, especially the punches for the dies or plates, were finished and tempered by the wire-drawer in his own home after his day's work. The wire produced by this method suffered from a poor surface finish and gauge tolerance, as judged by modern standards, and only short production runs were possible.

The first move from single-hole wire-drawing came about 1900, with the initial introduction of multiple-die machines. The heavier variety of these machines, working at finishing speeds of up to 250 ft./min., produced finished wire direct from rod in one operation, while the lighter variety operated on inlet wires below about 0.080 in. and finished at 0.016 in. upwards; one of these machines is illustrated in Fig. 7 (Plate LVII). These developments brought with them several important changes. One was the use of chilled cast-iron plates

or dies, which could be re-sized or reconditioned with steel reamers, in place of the traditional hammer-and-punch method on steel-plate dies. Another was that owing to the slip between the wire and the capstans, consequent on imperfect synchronization of speeds and reductions, and the attainment of higher temperatures by the succession of reductions, the lubricant was called upon to act as a coolant to the wires being drawn. Incidentally, the new methods of wire drawing rapidly gave prominence to many of the problems relating to overwork, or the incorrect application of cold work, which had not been apparent when wires were drawn by the single-hole method.

The earliest types of tandem rod-drawing machines persisted for nearly twenty years after the turn of the century, the only noticeable progress being an increase in drawing speed to about 350 ft./min. The cone types of wire-drawing machines which were in use up to about 1920 had maximum speeds in the region of 750 ft./min. An example of such a machine is shown in Fig. 8 (Plate LVII).

3. Evolution of Modern Methods.

The important advances in speed achieved in the 'twenties can be ascribed mainly to the introduction of the tungsten carbide wire-drawing die, and in a later section this is discussed in more detail. This product of powder metallurgy, although slowly adopted by the wire-drawing trade, was the means of revolutionizing both the methods and machines used for producing the coarser gauges of wire, at the same time improving the quality and finish of the latter.

The period 1920–30 saw a continuous increase in drawing speeds, a development which was, however, limited by the design of the machines; but by 1930 several engineering firms specializing in wire-drawing plant had produced both tandem- and cone-type machines with finishing speeds of 2000 ft./min. The attainment of high speeds was a particularly urgent requirement in the drawing of copper, and in the ferrous trade speeds remained at a much lower figure. The machines for iron and steel wire manufacture followed a development pattern built around dry drawing and the linking together of a number of single-hole wire-drawing blocks so as to provide non-slip drawing (see Figs. 9 and 10, Plate LVIII). Such machines are favoured for several non-ferrous metals, including nickel and aluminium alloys, on which the slip type of machine may have deleterious effects. Only for the finer gauges of steel wire have wet-drawing machines, so well known in the copper industry, been employed.

A later development from this linking together of bull blocks—often shaft-driven from a common motor with suitable gearing, though also

frequently with individual A.C. motors—has been the construction of tandem machines of from 4 to 7 dies, with each capstan on a floating arm and individually driven by a D.C. motor, so that complete synchronization of speeds can be accomplished as between each of the dies. This development of non-slip types of tandem machines, for the particular purpose of steel wire drawing, is now having repercussions in the non-ferrous metals industry, at least for specific products.

Arising from the improved die life and increased operating speeds of machines was the desirability, and even necessity, of attaining continuous drawing by brazing or welding successive rods or wires together. Generally, resistance butt welding has become the standard method, though considerable time elapsed before this was applied to copper rod exceeding $\frac{5}{16}$ in. in dia., and even to-day butt welding is not universally applicable for the largest rods.

The continuous-drawing practice in turn, owing to the high tonnages of wire produced by a single machine, involved the use of a central-reservoir lubricant system, so as to prevent excessive trough lubricant temperatures, and also to enable the wires drawn to be kept as cool as possible.

All these factors combined to render necessary the development of a new wire-collection technique. Whereas wires were previously taken from the machines in coil form and later rewound on to drums or spools, the new methods involved collecting by spooler units, in the case of finished wire direct on to the type of spool or drum packet required.

II.—PRESENT-DAY PRACTICE.

In Sections IV and V detailed consideration will be given to the practice followed for specific non-ferrous materials, but there are certain fundamental features common to machines and methods, and these will now be reviewed.

By 1938 it can be said that the present-day type of machine had been evolved. Though design has, of course, advanced and improvements of one kind and another are continually being introduced, enough development had occurred to fix the broad technique now existing in this and other countries.

First, in regard to die materials and die design, the general practice in the non-ferrous metals industry is to employ tungsten carbide down to sizes of 0.055 in., generally and sometimes as low as 0.040 in dia., and to use diamond dies for all lower sizes. The upper limit of the dimensions for diamond dies is generally 0.064 in. dia. As far as practicable there is complete segregation of tungsten carbide and diamond dies in

machines, though this is not a fixed rule and in the production of finished material direct on tandem machines it is a frequent practice to use diamond for the finishing die.

Extensive studies of die design were made by Thompson and others

(a) For Copper Wire.

Die Dia., in.	Bearing Length	Back Relief
0.050-0.250	100-50% of dia.	15% N.H.

(b) For Copper Wire.

Die Dia., in.	Bearing Length	Back Relief
0.250-0.516	50-25% of dia.	15% N.H.
0.517-0.750	40-30% of dia.	"

(c) For Low-Carbon Steel.

Die Dia., in.	Bearing Length	Back Relief
0.006-0.015	50% of dia.	0.005-0.010 in.
0.016-0.128	"	15% N.H.
0.129-0.230	"	"
0.231-0.516	$\frac{1}{4}$ in.	"
0.517-0.750	$\frac{1}{8}$ in.	"

(d) For High-Carbon Steel.

Die Dia., in.	Bearing Length	Back Relief
0.006-0.015	66% of dia.	0.005-0.010 in.
0.016-0.128	"	15% N.H.
0.129-0.230	"	"
0.231-0.516	$\frac{1}{4}$ in.	"
0.517-0.750	$\frac{1}{8}$ in.	"

N.H. = Nib Height.



FIG. 1.—Die-Angles and General Dimensions of Tungsten Carbide Dies.

over 20 years ago, and it is of interest to note that the present-day schedules of shapes and dimensions adhere closely to those then confirmed as being the most efficient. Fig. 1 shows the die-angles and general dimensions of tungsten carbide dies used for drawing copper and steel, the latter being given for comparison purposes. Fig. 2 gives

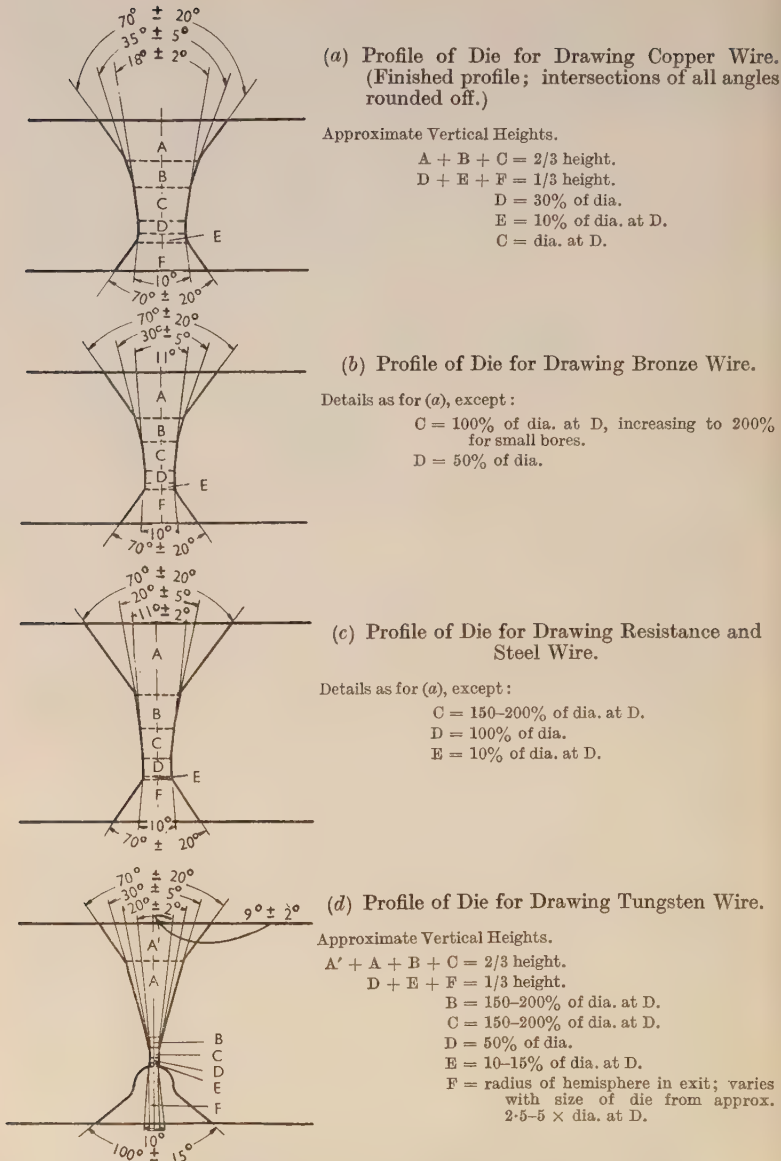


FIG. 2.—Die-Angles and General Dimensions of Diamond Dies.

KEY: A = Entrance; A' = Bell; B = Approach; C = Reduction angle; D = Bearing;
 E = Relief; F = Exit.

similar information in the case of diamond dies used for drawing copper, bronze, steel, and tungsten.

The use of correctly shaped dies is most important in order that the wire shall be worked uniformly throughout the section. If die-angles are too great, then the cold-working effects are not transmitted to the centre, the result being a heavily worked surface and a somewhat softer core, which later leads to internal fractures of the "cup-and-cone" type. If die-angles are appreciably below those recommended then there is excessive friction, with high power consumption and possibility of wire breakage by tensional effects.

The differences in die-angles depicted in Figs. 1 and 2 for the dies employed for the various metals are associated with this question of the transmission of cold work throughout the particular section being drawn, since it is found that some materials transmit the cold-working effects more easily than others. In general, the softer the metal being drawn, the greater the angle of the die. The "bearing" lengths are dependent on the frictional effects between the metals and the dies; clearly a compromise must be made between the life of the die at the tolerances permitted and the frictional effects which can be tolerated. The bell angle is of minor importance, but the back relief shape must be such that the expansion of the drawn wire, when it leaves the die, can be accommodated. Thus with the hardest metals, such as tungsten, the back relief shape is very different from that used in the dies employed for copper and similar metals.

Considering the range of metals fabricated into wire, it is surprising that such close similarities of die design and reductions are possible for the different metals. Thus, it is the practice to produce hard alloy steel wire with reductions of 20-25% per draft, just as is often the case with the softer non-ferrous metals. For the austenitic stainless steels there are records in the literature of reductions of 50% of cross-sectional area being made in the first draft following annealing, and this figure approaches the maximum which can be undertaken with any of the non-ferrous metals.

In the course of the evolution of present practice, the reductions effected per draft and the total reductions between annealing operations have varied a good deal; however, the outstanding trend has been towards standardized reductions per draft of the order of 20-25%, and seldom exceeding 30% in the case of any of the non-ferrous metals. Annealing has been eliminated wherever possible; at the present time copper is drawn hard throughout all stages from the rod onwards, whereas at one time with single-hole wire-drawing practice there were several inter-stage anneals.

The number of reductions effected on a single machine of the tandem or cone type has varied widely. Some designs of cone machines were built to accommodate as many as 25 dies, but the modern trend has favoured a reduction, and generally the number now ranges between 12 and 17. Tandem machines have between 5 and 11 dies, according to the size of product being made.

To suit the particular class of work involved, there has been a widening of the range of machines, and the standard method of classifying machines into tandem or heavy, medium heavy, medium fine, and fine wire-drawing machines is to-day not quite sufficiently comprehensive; in particular there are several classes of heavy machines.

The speeds of machines, attained by 1938 and not sensibly modified since, are of the order of 1500–3500 ft./min. for the heavier- and lighter-gauge products from tandem machines and from 5000 ft./min. up to as much as 8000 ft./min. for medium-fine machines. It may be pointed out that, with the use of extra-large-diameter take-off reels, higher speeds have been attained, namely 5000 ft./min. for tandems, and 12,000 ft./min. for medium-fine machines. Incidentally these latter speeds were attained in the early 'thirties, and the tendency subsequently has been to reduce speeds.

Most modern machines are powered with A.C. motors having variable-speed gear-boxes, generally with three speeds. With design based on the transmission of power with minimum losses, the engineering standard of the modern machine has reached a high level. Naturally the diameter and speeds of the capstans are related to the reductions effected per draft, and these ratios must be maintained. Great amounts of wear on capstans, and the use of any drawing schedule far removed from the initial lay-out as the result of wear of dies or other causes, must be guarded against if excessive slip is to be avoided. Some wire slip is inevitable, and within limits this is quite tolerable.

While it is thus general custom to employ the slip type of machine, the application of heavy non-slip tandem machines has been a feature of certain modern plant lay-outs. The reasons for this are associated with the adoption of heavier-gauge wire-rod for the manufacture of special products, such as heavy-section wire, high-surface-quality wire, and large-diameter round wire, e.g. for rivets, from either an extruded or rolled base. As previously mentioned, these non-slip machines have individual D.C. motors for each capstan, and the floating arms on which the latter are mounted effect the required synchronization. In the case of copper it is a common practice to use one of the stages for rod shaving, a process by which about 0.008 in. of the skin of the metal is removed, and which is reputed to give a superior surface. Non-slip drawing

practice has not been taken up with complete enthusiasm for the drawing of copper because of the greater cost involved. For some other non-ferrous materials it might be expected to make greater headway.

III.—DIE MATERIALS, MAINTENANCE, AND PERFORMANCE.

1. *Tungsten Carbide Dies.*

The introduction of tungsten carbide dies has been the most outstanding single contribution to wire-drawing practice, and therefore deserves detailed attention and particular reference to the initial difficulties.

At first only small pellets were available, of a maximum size of 13 mm. dia. \times 9 mm. in height, while a common size was 9 mm. dia \times 6 mm. high. After drilling, these pellets had to be brazed into a steel case, so as to provide overall support, and to make a convenient size of tool for handling and fitting into the die-holders. Many of the early dies were of variable quality, and shared a common fault of porosity. When drawing copper, this porosity caused die loading, resulting in a draw-lined surface, and also leading to wire breakages. In addition, owing to faulty casing many of the pellets fractured during use, and these factors, combined with opposition from the operatives, made their general acceptance in non-ferrous wire-drawing mills a fairly long process.

In connection with the porosity and tendency to encounter die loading—i.e. the occlusion of metallic and oxide particles in the open pores with a consequent dragging or galling effect if drawing is continued—it is of interest to note that the performance of tungsten carbide dies for the drawing of copper or aluminium has never been as satisfactory as in the case of steel drawing. It is surmised that the soft metals have a tendency to fill the microscopic porosities present in the dies and in so doing to tear out and carry with them minute particles of the tungsten carbide, thus aggravating the condition. This conception permits an appreciation of the varying performance of individual dies according to the porosity present. It also follows that the development of a more perfect medium for the tungsten carbide particles would result in a better performance in the drawing of soft metals. Work on these lines has recently resulted in the claim that a greatly improved life is attainable and the useful range of sizes can be broadened say down to 0.030 or even 0.020 in. dia., though actual trials do not appear to have been conducted.

The first pellets were of solid form and needed to be machine pierced before opening to the size required. The latter operation was usually performed on horizontal- or vertical-type multi-head machines, the

final sizing and shaping being done by hand. This was an expensive process, and necessitated an increase in die-room plant and labour. However, the greater production of wire, with lower labour costs in drawing, more than offset these other factors.

Improvements in the method of manufacture, especially in the sintering processes, gave better and more uniform control of the pellet shrinkage, and the first rough-cored dies were introduced at a very early stage in the history of tungsten carbide dies; these were usually made by shaping and drilling in the pre-sintered stage while the product was in a friable state. Studies on the ball-milling and compacting

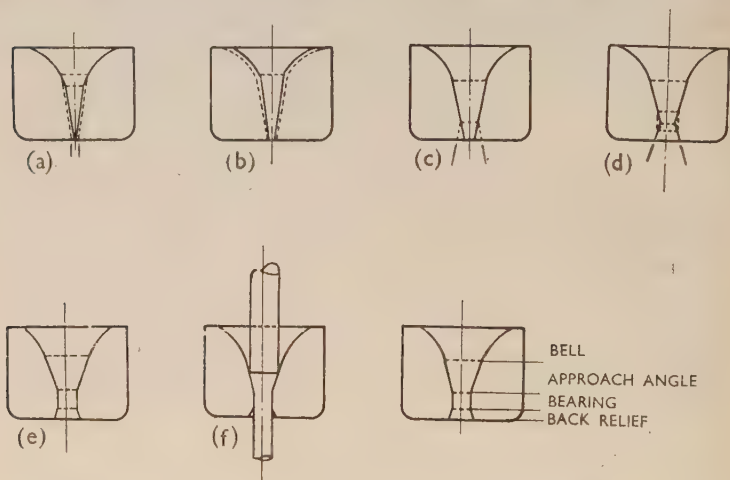


FIG. 3.—Stages in Making a Tungsten Carbide Die from a Rough Cored Pellet.

processes led to further improvements in quality, so that most of the objections to the earlier pellets were overcome, and with a gradual increase in size of pellet or bar capable of being produced, the utility of the product widened.

The hot-press method of manufacture rapidly followed, giving increased density and a finer degree of accuracy, and yielding eventually prepared dies of a better polish and wearing quality. This method widened the scope of tungsten carbide dies to make possible their use for tube-drawing and other purposes. A problem, with large sizes, is the sintering technique, involving careful control of sintering speeds and temperatures so as to obtain a uniform shrinkage, a difficult matter where the mass in relation to the dimensions is small; with normal sintering methods the contraction allowance can be as high as 23%.

An extension of the technique has enabled the production of square, hexagonal, and rectangular dies, which are now influencing machine design for section wire production in the same way as the tungsten carbide round-wire dies affected the machines of their day.

The standard size of tungsten carbide pellet for normal wire-drawing dies now extends up to about 45 mm. dia. \times 40 mm. high, there being a range of sizes to suit different sized machines. Fig. 3 shows the stages involved in preparation of a die from a rough-cored pellet.

After completing their useful lives at the initial sizes, the dies are opened out by rough turning with a diamond splint or tool, and then ground with carborundum abrasive and/or diamond dust in at least two operational stages. The first grinding is with a tapered steel needle, but the final polishing is conducted with a piece of the appropriate wire oscillating in the die. The total useful life which can be obtained from an individual die is difficult to assess, as this depends on the ratio of actual wear to the discard by turning and grinding, but it is obviously considerable. In practice each die is identified by a number, and card records are maintained of the performance at each stage, from the initial size until the die is opened out to such an extent that further use is impossible. Thus a statistical analysis is available which enables a spot check to be made of the various factors contributing to die wear, though all too frequently the reasons for abnormality are difficult to elucidate.

2. Diamond Dies.

In non-ferrous wire fabrication, diamond dies are used for the finer sizes, say, below 0.050 in. approximately. The use of precious stones for this purpose dates back for countless years, yet the large-scale use of diamonds only coincided with the industrial developments of the nineteenth century. The advantage of the diamond is its hardness and long life under onerous working conditions. The die sizes in everyday use are from about 0.064 down to 0.0004 in. dia., the latter for filament wires. In the copper industry there is little call for products even as low as 0.001 in., but lower sizes are well within the bounds of possibility.

Methods of diamond-die manufacture are outside the scope of this paper, but these, and also the die-maintenance operations, are most important phases. Diamond dies for a given machine production are kept in sets, and close records of reconditioning, &c., are made, as is the case with the tungsten carbide dies.

3. Wear of Dies.

Most dies in ferrous and non-ferrous wire drawing show the same wear pattern, finally manifesting itself as a draw-ring, which so increases

the frictional effects that wire breakage rapidly follows. There are many factors contributing to die wear, and amongst these are :

- (a) Unsuitable or insufficient lubricant or coolant.
- (b) Foreign matter rolled into the wire.
- (c) Poor pickling practice or insufficient washing.
- (d) Speeds, temperature, and reductions in drawing.
- (e) Die design, i.e. angles of entry and extent of "bearing".
- (f) Variations in quality of die material.

In practice the maintenance of dies has developed into rather a routine matter, as it is far better to take dies out of service for polishing and reconditioning before they have reached the stage when the wire

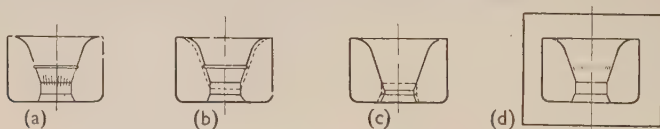


FIG. 4.—Observations on Die Reconditioning.

- (a) Die left in service too long.
- (b) Common method of repair, leading to incorrect angle with too short a bearing. This die will produce faulty wire.
- (c) Shows die correctly repaired and illustrates loss of carbide arising out of condition (a).
- (d) Correct condition of die when withdrawn for reservicing. A simple polishing operation allows the die to be put back into work without loss of die stock and at approximately the same diameter as when withdrawn.

product is out of gauge or shows other defects. In the latter instances it will usually be found that the dies have been damaged, as for instance by excessive rings, with many grains pulled out, or by excessive score marks. This point is brought out in the series of sketches given in Fig. 4, which show how the development of a die-ring results in an undue loss of die material besides the considerable time involved in opening out the diameter.

IV.—FABRICATION PRACTICE FOR COPPER.

1. General Methods.

British practice in the production of copper wire has long been standardized on the use of wire rods of 0.25 in. dia., though for certain products wire rod of 0.31 in. or greater is employed. The raw material for wire-rod production is the horizontal-cast tough-pitch copper wire-bar of a standard weight of 250–275 lb., though sometimes 550 lb. wire-bars are employed. In the period before the development of tungsten carbide dies, the standard weight of wire-bars was 135 lb., and there may be a definite connection between these two developments.

Certainly in the days when steel plate and chilled iron dies were employed, about 135 lb. was the maximum weight of metal that could be drawn without the necessity of changing dies owing to wear.

In addition to the horizontal-cast tough-pitch copper bars there are special varieties, namely vertical-cast (V.C.) tough-pitch, scalped horizontal tough-pitch, and vertical-cast oxygen-free. All these have greater ductility and other associated advantages due to the fact that they are free from the concentrated oxygen-rich zone which is a feature of the horizontal-cast bars.

Wire-bars are processed by hot rolling to give wire rod of 0.25 and 0.31 in. dia., as the standards, but larger sizes are also produced for the particular purpose of drawing to heavy-gauge round and section wire. In addition wire rods are produced by extrusion, though the tonnage is small and the method is mainly confined to wire required for particular purposes, such as heading.

Rod-rolling practice exerts a great influence on the quality of copper wire, and it is essential to perform this process under favourable conditions and in particular to avoid fins at any pass. Partly to reduce the incidence of the effects of roll fins, and partly to remove the zone which is rich in oxygen (from the original set surface) the rod-shaving process was developed. Owing to cost, however, it has not made great headway.

2. Machine Practice.

For the production of wire of the normal sizes, the hot-rolled wire rods, after pickling and washing, are drawn on tandem machines, usually provided with from 5 to 9 dies (see Fig. 11, Plate LIX), and undertaking reductions per draft of between 25 and 30%. The products from these machines range in size from 0.052 to 0.128 in., and the tonnage output depends on both size and finishing speed. Collection is mostly by reels (see Fig. 12, Plate LIX), and one of the most important measures in the last few years has been the standardization of reel sizes at individual works. Representative modern practice is to collect on reels of 2 tons weight for 0.128 in. dia. wire and 600–800 lb. weight for about 0.060 in. dia.

Following the tandem machine process, the wire, if not yet of finished size, is drawn on medium-heavy or medium-light machines in which from 12 to as many as 21 reductions are performed. Figs. 13–16 (Plates LX and LXI) show views of typical modern machines in these categories. These machines are all of the cone type, and they do not call for individual comment, except in the case of Fig. 15, where the provision of concentric shafts to each of the capstans enables the diameters of the latter to be kept constant. The normal reductions

effected at each die on all these machines is of the order of 26%. The collection of wire from these machines is performed on reel sizes of 200 lb. for metal about 0.030 in. dia., 60 lb. for metal about 0.010 in., and 20 lb. for finer sizes. In further processing the reel size is progressively reduced. For the drawing of the finest sizes of wire it has

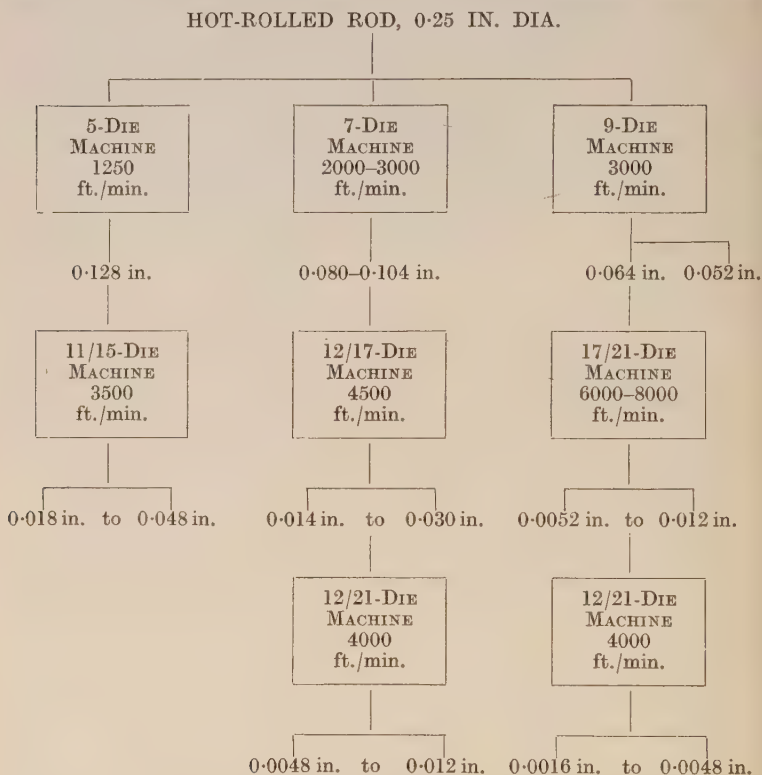


FIG. 5.—Flow Sheet Representative of Normal British Practice.

in the past been unusual for the machines to be of the totally enclosed type, and the lubricant is conveyed only to the die holders which have a traversing motion. Fig. 18 (Plate LXII) shows a group of such wire-drawing machines. Fig. 17 (Plate LXII) shows one form of flaking take-off for fine wire.

Fig. 5 gives a flow sheet of what may be described as representative modern British practice, and it will be observed from this that it is possible to reduce to a size as low as 0.0052 in. in two machine operations.

While at the tandem stage, the aim is to obtain continuous working

by butt welding; in the fine-wire stage of operations the time required for consuming an inlet reel, weighing several pounds, is so great that the welding of successive reels is not adopted. The break in operations gives an opportunity of polishing the faces of the capstan rings. If the latter are allowed to get into bad condition by grooving due to the action

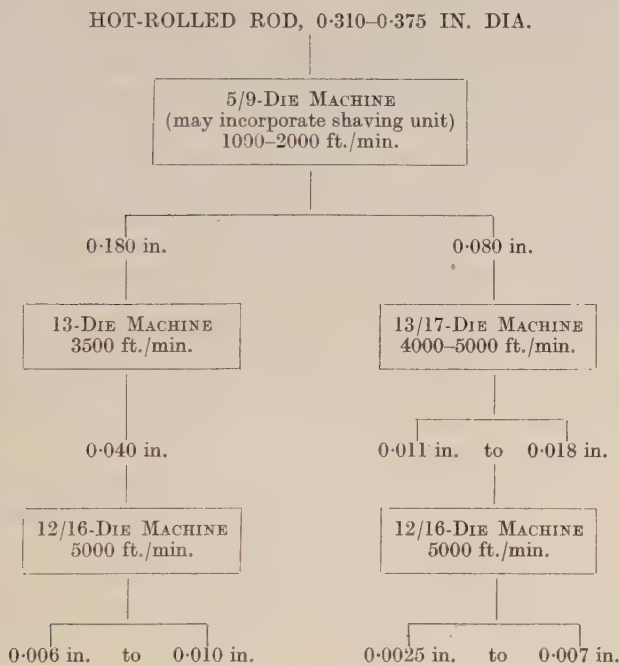


FIG. 6.—Flow Sheet Typical of Current U.S. Practice.

of the wire, then the wire quality is adversely affected; a few minutes' polishing after completing the reel is considered well worthwhile. Tungsten carbide has proved extremely satisfactory for the smaller capstan rings, as it has been found that at least one year's service can be obtained without signs of grooving.

3. Comparison with American Practice.

In contrast with the British unanimity in regard to the use of wire rod of 0.25 in. dia., American manufacturers are divided, some using 0.25-in.-dia. and others 0.31-in.-dia. stock material; it would appear

that the latter practice now predominates. It is argued that under American conditions it is more economical to obtain the higher output from the rod mill, i.e. about 20% greater, and to provide the additional wire-drawing equipment. In arriving at decisions about rod-size, quality has been one of the factors considered and in particular the merits of rod shaving have been advanced, it being obviously best to perform this on the larger-diameter material. However, the proportion of products shaved is negligibly small.

In American wire-drawing practice, it is almost a universal feature that machines are designed on the basis that each draft is of one Brown and Sharpe gauge, i.e. 20·7% reduction. All products are made to gauge numbers, and the adherence to this rule tends to simplify the industry. However, it means that the total work performed in a particular machine process is not as great as it might be, at least with such a ductile metal as copper. Some of the heavier machines are designed to effect one and one-half B. & S. gauge reductions per draft, though this practice is not very common.

A comparison of the flow sheet in Fig. 6 with that in Fig. 5 brings out the points of difference between American and British practice. In particular, it can be seen that for a range of sizes it is British practice to produce in two machine operations, whereas American practice requires three operations.

One point which may be noted is that American users favour the cone type of machines for quite heavy sizes, whereas in British works tandem machines would be used. More specifically, there is a 13-die cone machine with an inlet size up to 0·25 in. from which the outlet size is about 0·057 in. British wire drawers would use a tandem machine having fewer dies and undertaking much heavier reductions per draft.

4. Lubrication.

In the drawing of copper, copious supplies of lubricant are required, mainly because it is essential to provide adequate cooling, and in consequence it is almost the invariable practice to employ a central system. Each of the machine groups, heavy, medium-heavy, &c., must have a separate system, generally also with a different fat content in each, about 7% for heavy, falling to 2-3% for the fine-wire machines. A feature of these systems is the provision made for the copper particles to be settled out before the lubricant is returned to the wire-drawing machine. The heavier particles rapidly sink, and the finer particles are separated in the storage tanks by means of baffles. It is, however, a

fact that the lubricant liquor always carries in suspension a proportion of micron-sized particles which are incapable of being filtered out, and do not settle even if samples of lubricant are left to stand for long periods. It is assumed that copper particles adversely affect die wear, but little work has been done to substantiate this. It is certain that finely divided particles of copper oxide in poor lubricants will act as an abrasive, but the exact behaviour of good lubricants with a micron suspension of particles is problematical.

Conditions which affect central lubrication systems are the quality of water, the size of reservoir capacity, whether cooling capacity is great enough in relation to the speed of drawing, and foam generation as affected by machine design and other factors. It cannot be said that any of them are really critical, as most wet lubricants are in the region of 90% water. The quality of water used in preparing the lubricant is important, excessively hard water causing precipitation of soap in the lubricant so that the stability of the fat emulsion is affected. This tends to clog the dies, if not the pipelines, and interferes with cooling and lubrication, with the result that surface particles from the wire are retained in the bell and throat of the die, resulting in greater die wear.

Acid water, however soft, is extremely bad for lubricant making, and a soft water in the region of 8.5 pH is more satisfactory. Low pH values give excessive copper soap, with clogged dies and lubrication pipes, &c., culminating in wire breakage on the machines.

5. Residual Lubricant on Metal.

The retention of lubricant on the surface of hard-drawn wire does not generally arise as a serious problem, though for a few products it is desirable to remove this as far as possible. Removal may be attempted by arranging for a snuggler of string or felt, soaked in spirit, to make contact with the wire after the last die and before the winding operation; however, on account of the speed of drawing this procedure does not afford time to remove all traces of grease.

For products marketed in the annealed condition the question of residual lubricant on the wire is one which cannot be lightly dismissed, because of the contribution which this can make to the staining problem. The incidence of staining is determined mainly by the atmospheric conditions in the bright-annealing furnace, but the composition of the lubricant is of paramount importance. Although this matter will not be discussed here, there is fairly general agreement in the copper industry that it would repay further investigation because of the heavy financial losses due to staining and other causes in annealing.

6. Annealing.

Inter-stage annealing is not now generally practised, as it has been found possible to draw from 0.25 in. dia. down to as low as 0.001 in. dia. without its being necessary. However, for some purposes inter-stage annealing is required because of the directional effects which exist in the annealed metal obtained after a heavy reduction. The modified industrial practice now current has tended to give annealed wire with a greater tensile strength and a lower elongation than was formerly the case when inter-stage annealing was adopted.

The final annealing operations on wire are always performed in one of the various types of bright-annealing furnace, but the matter will not be considered in detail here. One important point is that wire tightly wound on reels will suffer from "stickiness" after the annealing treatment. One form of this trouble is the actual welding of adjacent turns of metal, probably as a result of the fact that the reduction of their surface oxide films is accompanied at a few points by spreading of the crystal grains in one wire across into the adjacent wire. A more usual form of stickiness is due to the entrapment of windings during the annealing process, and the use of a smaller tension at the winding stage following drawing often suffices to put matters right; however, this reduction of tension can be achieved only at the expense of output.

7. Continuous Annealing.

Until quite recently no practical success had attended any of the various methods which had aimed at the continuous annealing of wire in tandem with drawing. The production of a fully annealed product direct from machines has, however, now been accomplished on a satisfactory basis by electrical-resistance methods, the wire after it issues from the drawing machine being passed around contact pulleys suitably spaced and carrying the necessary current to heat the wire above the annealing temperature in a fraction of a second. Compliance with all the conditions has been far from an easy matter, but it would now appear that the problem of electrical pick-up without burning, avoidance of oxidation, uniformity of annealing, transfer of reels with wire running, and many other matters have been satisfactorily solved.

The use of continuous-annealing units as adjuncts to wire-drawing machines promises to reach an established position for copper and many of the copper alloys, there being particularly marked advantages in the latter case. However, the universal application of this method may take some time.

8. *Rectangular and Section Wire.*

Rectangular wire is usually required in such small quantities that drawing by machine is uneconomic, and for this reason bull-block drawing is the normal method. However, for large quantities machine drawing is justified, while it may be noted that in the U.S.A. there has been such standardization of rectangular wire sizes that in some factories tandem rolling with both horizontal and vertical rolls at finishing speeds up to 1000 ft./min. is the present routine.

In place of individual rectangular dies, use has been made of dies built up on the Turk's head principle, and the application of tungsten carbide inserts in these adjustable dies has been most useful.

If a greater measure of standardization of sizes could be secured in British industry, then there is every reason to believe that the machine drawing of rectangular sections or the application of combined rolling and drawing would make rapid headway.

Trolley and contact wire, with a cross-sectional area up to 0.3 in.², is a special form of wire product for which plant of a heavier nature than has so far been considered is necessary. Modern practice is to produce the finished section from hot-rolled stock in one machine operation equipped for between three and five drafts, and finishing at a speed of the order of 200 ft./min.

V.—FABRICATION PRACTICE FOR OTHER MATERIALS.

1. *Conductivity Bronzes.*

In British industry, the only important material under this general heading is cadmium copper, containing upwards of 0.7% cadmium, balance copper. However, until a few years ago the standard alloy was a copper-tin bronze having a composition of 1.0% tin, balance copper, and bronzes of a rather similar composition, often containing small amounts of other elements in addition, are well known in some other countries.

Wire drawing of the above qualities is accomplished by methods identical with those employed for copper; for example, cadmium copper can be drawn to about 0.060 in. dia. in one machine operation from the usual rod size of 0.375 in. dia. A point of metallurgical interest is that the highest tensile strengths can be attained only by drawing on machines with large-diameter capstans; the use of small-diameter

capstans apparently reduces the directional effects, which it is necessary to retain for maximum strength purposes.

2. Copper-Zinc Alloys.

The industrial brasses which are fabricated into wire mostly lie around the α - β phase-boundary limit, so that they have a composition of 62-65% copper; lead is sometimes desired in amounts up to 2% in order to improve machining characteristics, but generally this element is restricted to below 0.5%, and sometimes below 0.1%, because of its adverse effects on ductility. Within this approximate range of composition the trade recognizes many commercial materials, classified according to the purpose for which they are intended, such as pin wire, screw wire, nipple wire, riveting wire, and many others. Outside this range there are alloys of higher copper content, possessing greater ductility and better corrosion-resistance, so that they are used for such typical applications as large-headed rivets and gauze wire; the most notable of these alloys is 70 : 30 brass. There are also other alloys, notably the 80 : 20, 85 : 15, and 90 : 10 brasses or gilding metals, which are used because of their colour or the fact that they can be brazed more easily owing to their higher melting points. For the so-called bronze-welding rods or wires, a number of special proprietary alloys of copper contents below 62% have to be fabricated.

The above is only a short summary of the position regarding compositions, and there are many other proprietary materials which may be required in wire form. Naturally the fabrication of such a wide range calls for differences in treatment, if only for the simple reason that their capacities for cold working are different. This latter feature imposes limitations on the extent to which the harder brasses, having a copper content below 62%, may be drawn.

Until twenty years ago a wide variety of initial working processes were in vogue for obtaining wire rods to be used as the stock for feeding wire-drawing machines. One recognized procedure was to cast a long bar of small cross-section, having typical dimensions of 5 ft. long \times $1\frac{1}{2}$ -2 in. square, and to cold roll this in grooved rolls to approximately 0.5 in. dia., with appropriate intermediate annealing; at this stage the product was suitable for drawing on heavy bull blocks. Another procedure, which was restricted to the brasses having a copper content around 62%, was based on the hot rolling of strip ingots down to about 0.10 in. thickness, followed by slitting of such strip into approximately square section and welding to give a coil of material which could be drawn. A modification of the latter method was the initial production of sheet, from which a slitting was cut as a spiral, beginning at the outside and finishing close to the centre, thus providing a fairly long coil for drawing purposes.

These practices have been abandoned by most manufacturers, though they are not entirely obsolete. In their place, the extrusion process is now employed for giving wire rod. The availability of extrusion plant and the general economics of production have formed only part of the story in this change-over, as quality of product has also been most important. The diameter of wire rod obtained from the extrusion press may be as low as 0.22 in. but manufacture of this small size is somewhat costly and generally the diameter is 0.30 in. or larger; it is purely a question of evaluating the extra costs of extruding to the small size as compared with the costs of cold drawing.

The wide variation in the stock of wire rod, coupled with the extremely wide range of finished product sizes, renders brass wire drawing a much less standardized procedure than copper wire drawing. Nevertheless, there has been a pronounced movement towards the adoption of machine drawing on tandem and cone-type machines. While some machines, for finishing wire in the range 0.016–0.036 in. dia. approximately, are of the 12- to 17-die type, there are a number of machines performing only 4 to 8 reductions per process.

The amount of work performed in each reduction averages approximately 20% reduction in cross-sectional area, and it is fairly general custom to effect total reductions between anneals of the order of 80%. at least with the brasses of about 62% copper content and containing the usual commercial limits for lead. With more ductile qualities a greater number of drafts with a larger amount of total work may be undertaken. It should perhaps be pointed out that modern views in regard to brass wire practice, as also in the case of the rolled-metal industry, favour the use of high-purity raw materials rather than the cheaper low-purity materials, because the former permit of greater reductions between anneals, as well as greater speeds of working. The saving of annealing costs is an important offsetting item.

One further feature of brass wire fabrication practice may be mentioned, namely, the directional effects which persist in the final annealed products as a result of the heavy amounts of cold work applied previously. For headed products such directional effects must be avoided, and therefore drawing practice has to be suitably modified; this means that there must be a moderate final drawing reduction after the penultimate anneal.

3. Copper-Tin Alloys.

The tonnage of bronze wire manufactured is insignificant in comparison with copper, though the various grades of bronze wire are of quite considerable industrial importance. The two outstanding in-

dustrial uses are hard wire for spring applications and annealed wire for Fourdrinier cloth, and the wire-manufacturing lay-outs are designed for these two markets.

While there are three or more commercial grades of bronze or phosphor bronze, providing different mechanical properties, the fabrication practice for all of them is very similar. The wire-rod stock material is mostly produced by the cold rolling of cast bars about 5 ft. long \times $1\frac{1}{2}$ –2 in. square section, but within recent years the lower-tin alloys, of a controlled high purity, have sometimes been hot worked from billets into wire rod by both rolling and extrusion, which cut out a large number of intermediate anneals, and save both time and labour in fabrication.

The wire-rod stock of about 0.4 in. dia. is processed by drawing on bull blocks and eventually on tandem and cone-type machines, the practice being very similar to that adopted for brass. Again, the capacity for cold work is limited, but with care a large number of reductions, each of the order of 20%, can be undertaken without the necessity for intermediate annealing. In this connection purity plays an important part, and it has been found worthwhile to bear the extra costs of high-purity raw materials, if some of the intermediate annealing operations can be eliminated.

The attainment of continuous drawing on machines is secured by silver soldering successive coils of wire, and as the silver-soldered joints have good mechanical properties and also capacity for cold work, the elimination of the joints is not attempted. Emulsion-type lubricants are always employed in drawing on machines, and solid fat-base materials on bull blocks. A noteworthy development of the last few years has been the adoption of strand annealing in a non-oxidizing atmosphere for all annealing processes below say $\frac{1}{8}$ in. dia., and this has eliminated a large number of troubles previously encountered in drawing, owing to imperfect pickling and the presence of oxide particles.

4. Aluminium and Aluminium Alloys.

The competitive position of aluminium has resulted in a gradual increase in the application for conductivity purposes of the commercially pure metal and also some of the alloys, particularly those containing small amounts of magnesium and silicon which provide a higher tensile strength.

Aluminium wire can be drawn on the same equipment as copper or brass, and also on the non-slip accumulator type of wire-drawing machines employed in the steel industry. The latter have been in-

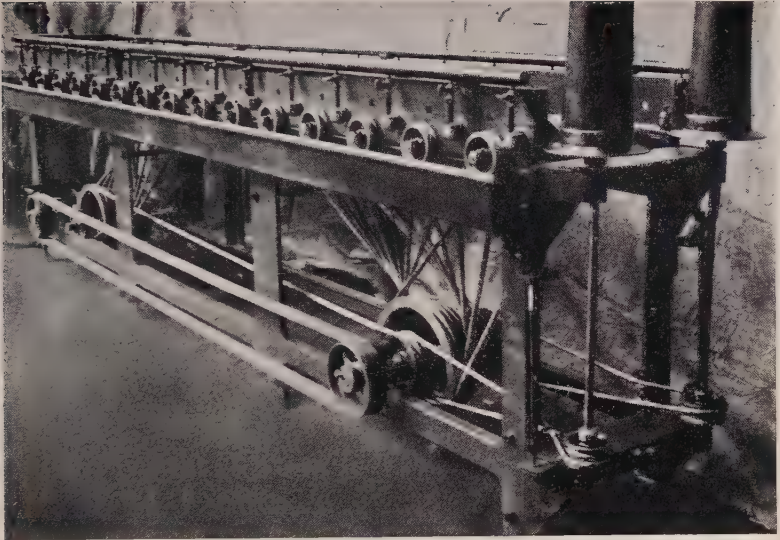


FIG. 7.—Fine-Wire-Drawing Machine as Employed about 1900.

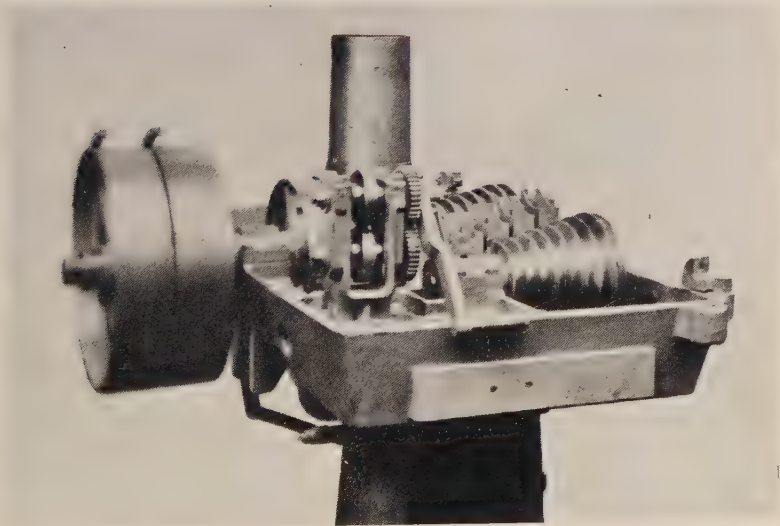
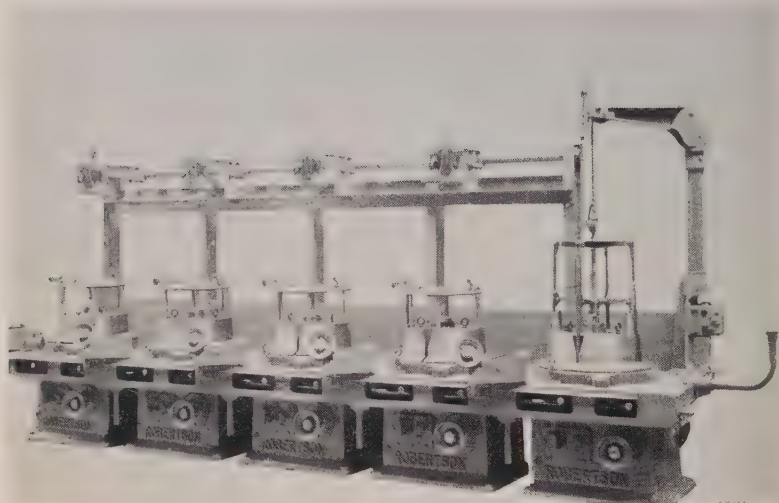


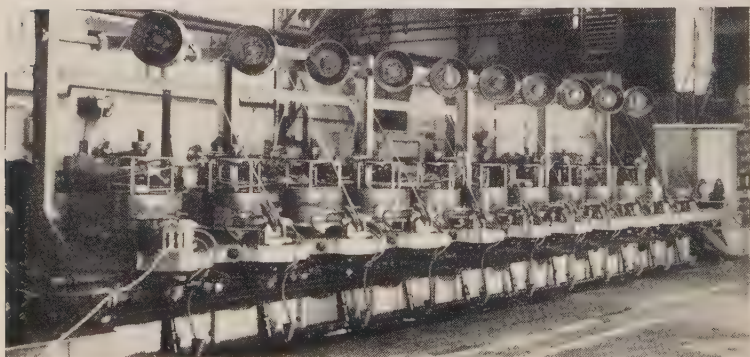
FIG. 8.—Early Type of Cone Drawing Machine.

[To face p. 558.]



[By courtesy of W. H. A. Robertson & Co., Ltd.]

FIG. 9.—A Series of Five Bull-Block Machines Arranged for Tandem Operation, and Providing Non-Slip Drawing.



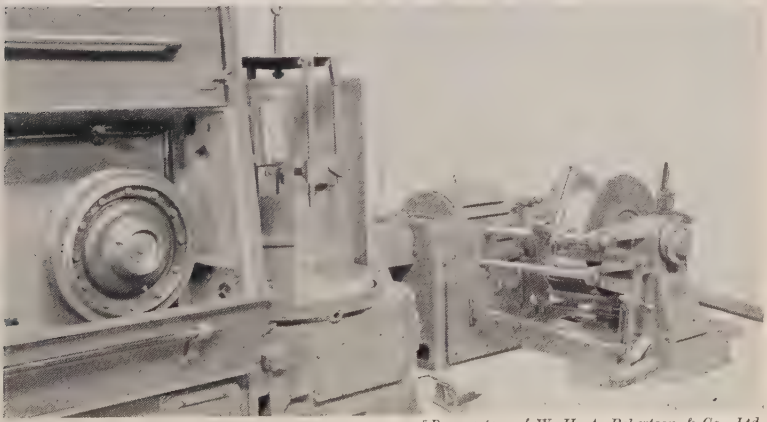
[By courtesy of Marshall Richards Machine Co., Ltd.]

FIG. 10.—Eleven-Block Machine, Used for Drawing $\frac{3}{8}$ in. dia. Aluminium Rod; variable finishing speed up to 1500 ft./min.



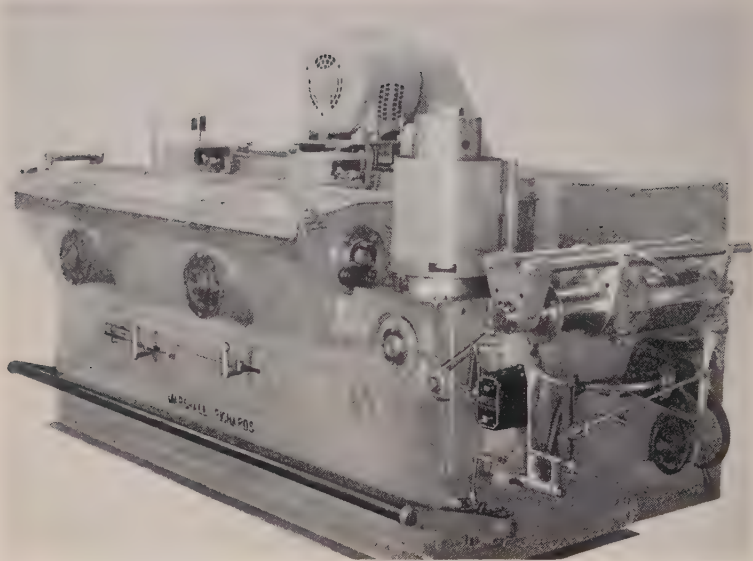
[By courtesy of W. H. A. Robertson & Co., Ltd.]

FIG. 11.—Seven-Die Tandem Machine for Drawing Heavy-Gauge Copper Rod.



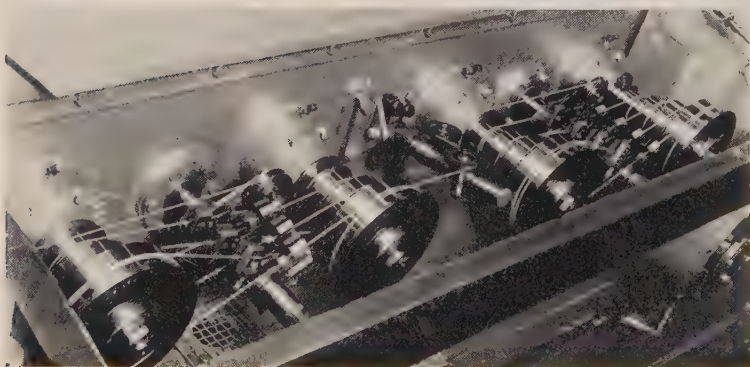
[By courtesy of W. H. A. Robertson & Co., Ltd.]

FIG. 12.—Details of Take-Off Arrangements for Either Coils or Reels of Typical High-Speed Tandem Machine.



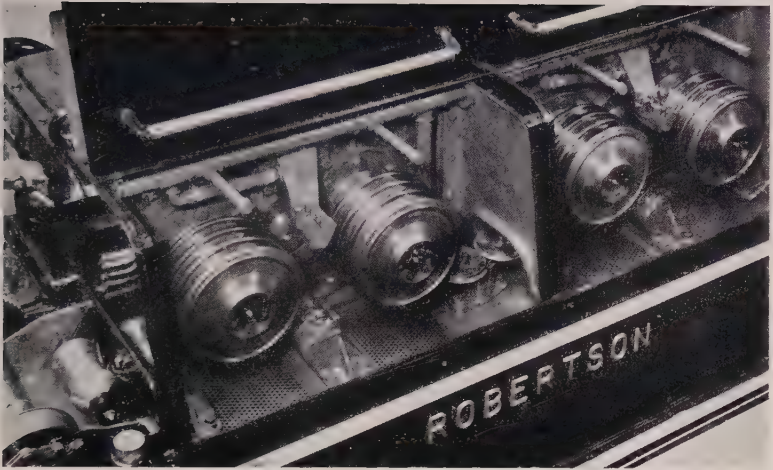
[By courtesy of Marshall Richards Machine Co., Ltd.]

FIG. 13.—Fifteen-Die Medium-Fine Machine.



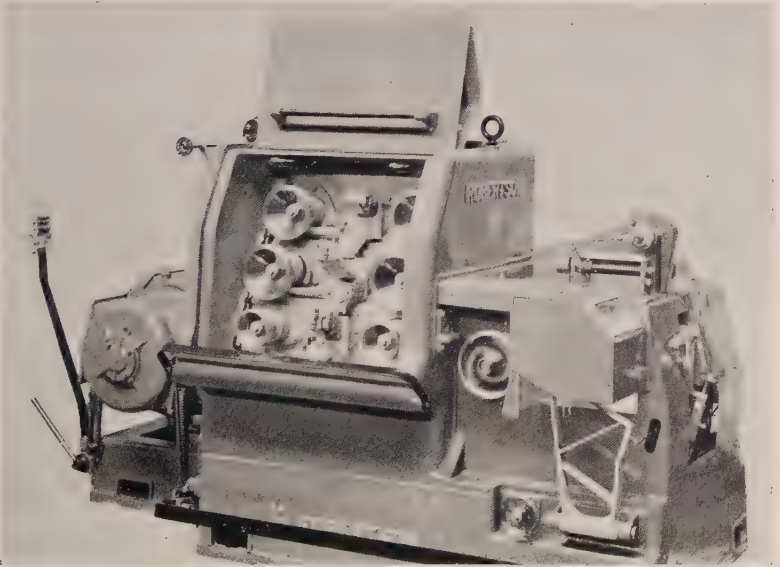
[By courtesy of Marshall Richards Machine Co., Ltd.]

FIG. 14.—Interior of Machine Shown in Fig. 13.



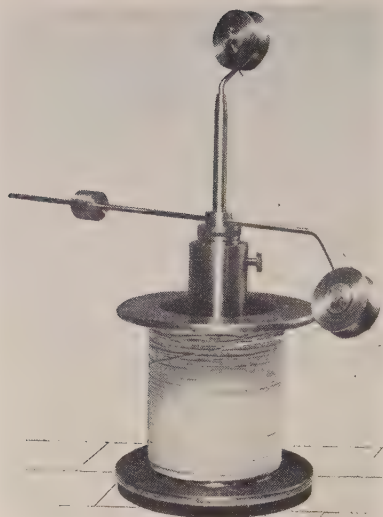
[By courtesy of W. H. A. Robertson & Co., Ltd.]

FIG. 15.—Close-Up of Thirteen-Die Medium-Heavy Machine, Provided with Concentric Shafts to Each of the Capstans.



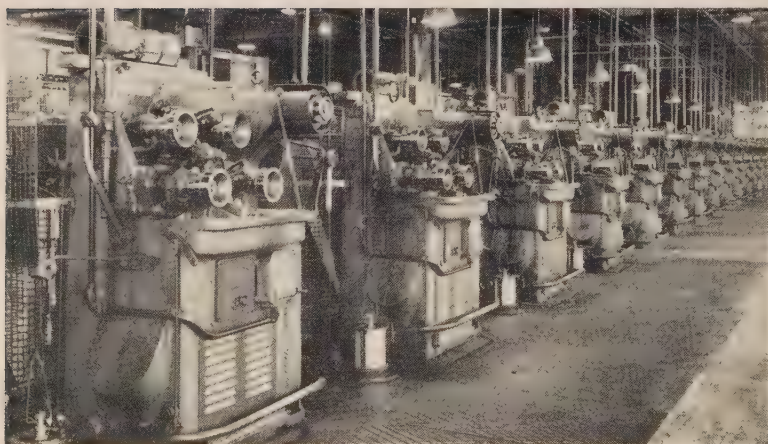
[By courtesy of W. H. A. Robertson & Co., Ltd.]

FIG. 16.—Medium-Fine Wire Machine with Twenty-One Dies, Operating on Copper Rod at a Speed of 8000 ft./min. Finished wire size range of 0.0048–0.012 in. dia.



[By courtesy of W. H. A. Robertson & Co., Ltd.]

FIG. 17.—Details of Fine-Wire Flaking Take-Off.



[By courtesy of British Insulated Callender's Cables, Ltd.]

FIG. 18.—Group of Machines for Drawing Copper Wire to Sizes 0·0016–0·0048 in. dia. ; finishing speed of 4000 ft./min.

creasingly used and have some definite advantages in the production of wires down to 0.093 in. dia., as they permit heavier drafting, cleaner drawing conditions, and more efficient wire cooling between dies. Finishing speeds up to 2000 ft./min. are common in this range, while it is on record that speeds as high as 4000 ft./min. have been reached in the U.S.A.

The lubricants generally have a vegetable or mineral oil base, when drawing on slip-type tandem machines, but many different recommendations have been made with the object of obtaining better lubrication properties, bearing in mind the presence of copious amounts of finely divided alumina particles. As may be appreciated, these particles can function in various ways, and at the best they are merely inert fillers.

In wire drawing at high speeds it has been found a distinct advantage to rotate the last four dies of a seven- or nine-die continuous tandem-type machine at speeds in the region of 400 r.p.m. This prevents metal pick-up in dies, to which aluminium is particularly susceptible, and improves the interfacial film qualities between wire and die.

Die practice is not greatly different from that in copper drawing; but the approach angle of 20–24° is slightly greater. The finish on dies must be extremely good, in which case very long production runs can be attained.

For fine wire-drawing, diamond dies are the most efficient. For drawing down to such sizes as 0.0076 in. on slip-type cone machines, good efficiency is obtained if the reductions per draft are limited to 15–18% for the intermediate range and 12% for the finer range. The reasons for this restriction in practice, in comparison with copper, would appear to be partly the greater frictional effects and partly the tendency of the metal to neck under low stresses, such as exist between each capstan and die. When necking occurs, then wire breakage will most probably result.

VI.—DEFECTS ENCOUNTERED IN WIRE PRODUCTS.

Many of the defects in wire making originate with the quality of the cast products or the rolled rod, but it is often difficult to determine the exact cause of the trouble.

Cold shuts, sloppy edges, and bad sets in horizontal-cast wire-bars, and the corresponding defects, as well as internal unsoundness, in vertical-cast materials, give rise to defects in the wire, these mostly taking the form of long slivers. In the course of hot rolling, the principal fault to guard against is the production of fins at any stage, due to bad roll settings, as these develop overlaps, giving rise to wire pro-

ducts with deep line defects and therefore possessing poor ductility. A further important point is that of guide settings, and if conditions are not perfect it is possible to experience an accumulation of metal which periodically breaks away as comparatively large particles which are rolled into the rod. Another defect is the rolling in of refractory or other foreign material, e.g. from wire-bar preheating furnace roofs. It has been established that such material can be one of the most frequent causes of wire breakage on drawing, and in some cases, where the rolled-in material is of a fine siliceous nature, extremely rapid die wear is experienced.

In the wire-drawing process itself, defects may be associated with machine conditions, such as the wear of capstans, resulting in actual damage to the wire or an excessive tension at one of the locations. Defects can also be due to die condition, and in this category occur the well-known "crow's foot" and "cuppy wire" faults.

Whereas "crow's foot" in copper wire was previously thought to be due to vibration effects caused by the use of heavy reductions in dies having unsuitable angles, so that the ingoing wire was damaged by contact with the mouth of the die, it is now realized that the original set surface of the horizontal-cast bars has a tremendous influence. With modern control methods the incidence of the "crow's foot" type of surface fracture is a rarity.

Cuppy wire is due to the use of dies with acute angles and short bearing surfaces, so that the wire is not cold worked evenly throughout the cross-section, the outer skin being worked more than the core. This ultimately results in the central portion of the wire developing internal fractures of a cup-and-cone nature—hence the term "cuppy" wire. It is a common experience that the defect is observed only at a late stage of wire production and not at the particular die which is defective.

VII.—DEVELOPMENT TRENDS.

Theoretical studies of the deformation occurring in the wire-drawing process have indicated that deformation would be accomplished with less power if both back pull and forward pull were applied. This was also demonstrated experimentally with low-speed drawing, and therefore for a long time the opinion was held that the industrial application of this principle would result in a definite advance. Many attempts to apply this principle, a matter of great difficulty, have been made, but the latest work on an industrial machine does not substantiate the claim, though it must not be assumed that the matter has been finally decided.

Another feature, on which high hopes had for long been built, was the rotation of dies; it was held on theoretical grounds that this would both reduce the power requirements and improve die performance. Industrial machines which have been developed with this feature have at least confirmed the better all-round die life and performance.

Many problems of die lubrication in conjunction with the deformation of the material remain to be adequately studied. Considerable work relating to die loading was carried out in attempts to apply the back-pull theory. The most severe die wear is experienced in the throat, or approach angle, of the die at the point of first contact between the wire and the die. This is expressed in the well-known drawing-ring effect, the severity of which depends on the nature and cleanliness of the material drawn, the quality and suitability of the lubricant, and the cooling conditions. Assuming that the dies in use have an original perfect shape and finish, it must be agreed that the wear rate is still severe. It might be suggested that much of the wear is due to frictional heat affecting the cobalt matrix as a result of imperfect lubrication, thus allowing the removal of the unsupported tungsten carbide grains, but the vibratory effect from the wire, especially at high speeds, is probably far more harmful. That die-wear rings are not a necessary feature of die wear has been demonstrated under actual production conditions by rotating dies at high speeds. In many cases the output of dies has nearly doubled in the tolerances specified, and they have shown no trace of wear rings at the first point of deformation. Dies which had previously been artificially draw lined, or made out-of-round and porous, have produced satisfactory wire and have been in a good polished condition at the end of drawing.

Little is known of the temperature set up in a die during the deformation of wire in its passage through the die, and some attempt to measure these values for different wire speeds and area deformation has been made. It must be pointed out that although the tungsten carbide die has made possible enormous increases in wire-drawing speeds, the wire tonnage per mil of actual die wear has fallen sharply with the increase in wire-drawing speeds.

The same factors of die wear and speed have been responsible for attention being directed again to the reductions effected at each draft, the object being to find the ideal reduction. On the one hand wire-mill personnel are anxious to achieve the maximum reductions at each machine operation, but on the other hand the design tendency in some cases is towards the development of machines in which the reductions effected are of a more limited amount. There is clearly a conflict of views on this point, but impartial consideration would indicate that it

is perhaps advisable to ensure a greater margin of safety against wire breakage than has always been the case in the past. It must not be overlooked that wire breakage brings down the performance of machines more than any other factor, but it would be bold to forecast the developments in this particular matter of ideal reductions and speeds.

While there is no doubt that machine design and performance have already reached a high standard, improvements in detail can be expected to continue. From a production aspect, one of the major lines of development is almost certain to be the linking up of wire drawing and annealing, and also perhaps of tinning.

ACKNOWLEDGEMENTS.

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THE DEEP DRAWING AND PRESSING OF 1290 NON-FERROUS METALS AND ALLOYS.*

By J. DUDLEY JEVONS,† Ph.D., B.Sc., F.R.I.C., F.I.M., MEMBER.

SYNOPSIS

The terms "sheet and strip" and "deep drawing and pressing" are commented on, and various methods of deep drawing and pressing are described. Crank and hydraulic actuation of presses are compared, and attention is drawn to certain merits of multi-punch presses.

Tool materials and drawing lubricants are classified, and the usefulness and limitations of each are explained. Inter-stage annealing is described with particular regard to the faults commonly experienced under industrial conditions and to the incidence of critical-strain crystal growth.

The properties of sheet which determine its behaviour under the press are discussed, and a nice balance between "tenacity" and "ductility" is suggested as being of primary importance in most instances. A number of ordinary and special tests applicable to sheet are described, and their limited usefulness in predicting behaviour under the press is explained. A method for the routine acceptance testing of sheet under industrial conditions is suggested. The phenomena of stretcher-strain markings and of season-cracking are reviewed and discussed.

Finally, the behaviour of those non-ferrous metals which are commonly deep drawn and pressed is described. A plea is made for closer co-operation between the supplier and the users of non-ferrous sheet.

I.—INTRODUCTION.

THE importance and extent of the part played by deep drawing and pressing in modern industry, as indeed in modern life, is seldom realized by those who have not made a special study of this particular process or, as it may indeed be called, craft. It offers what is often by far the least costly, and not infrequently the only practical, way of making on a quantity-production scale an enormous variety of thin-walled articles ranging in size from a tiny electrical connector less than an eighth of an inch in diameter, through a scale illustrated by cartridge cases, electric-lamp caps, tableware, kitchen utensils, food containers, to—turning for the first time to steel—such large articles as motor-car bodies and, in the United States, even baths and burial caskets.

Having regard to the extensive use made of this process, it is strange that until fairly recently it has received little scientific study, and that even to-day the design of tools and apportionment of stages in multi-

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draw sequences is still dependent much more upon experience and intuitive skill than upon the application of established rules or scientific data. From the metallurgical aspect the situation, although unsatisfactory, is not quite so bad, for extensive metallurgical knowledge, none the less welcome on account of the fact that it has been gained primarily for other applications, has been used to improve the quality of the sheet used in the press shop. Even here precise scientific knowledge is still lacking, for the exact properties, or rather combination of properties, which make sheet behave in the desired manner under the press have not yet been identified and cannot be measured.

1. *Definition of Terms.*

Sheet and Strip.—Some years ago the term “sheet” implied that cross-rolling had been applied during the latter stages of the reduction of an ingot into the finished product of a mill, whereas “strip” meant that all, or nearly all, the reduction had been accomplished in one direction to give a relatively narrow continuous ribbon instead of wide separate pieces. The advent of steel strip as wide as, or wider than, the sheets hitherto produced led to a loose application of the term “sheet” by users, a happening which will probably be repeated in the case of aluminium alloys now that wide strip mills are being installed for this light metal. The term “continuous sheet” has been proposed, but, judged by the criterion of cross-rolling, this is a contradiction in terms. It remains to be seen whether, in time, the user will adopt the more informative nomenclature of the supplier, or whether the gradual replacement of sheet by wide strip, which seems to be an established current trend, will ultimately render distinction unnecessary.

In this paper, which is concerned with deep drawing and pressing as distinct from the manufacture of sheet and strip, the metal shaped under the press will for the sake of both brevity and convenience be called “sheet” when spoken of in general terms not requiring special distinction.

Deep Drawing and Pressing.—Here confusion arises not so much from the fact, as with “sheet” and “strip”, that the wrong term is used by persons unaware of its true significance, but because no proper definitions have been generally accepted. The term “drawing” probably had its origin in the behaviour of a blank in the press during many operations of the kind under consideration, in which, as the periphery of the blank diminishes, it may well be said that the blank is “drawn” into the die. The significance of the word “deep” in certain instances will be obvious. “Pressing”, on the other hand, should logically be the shaping of sheet, for example by bending or by

causing the edges to flow so as to form a shallow cup, without the occurrence of the inward flow of the periphery of the blank of the kind just described. Unhappily the term has come to be applied to shallow products, even though the process by which they are formed is in fact a true "drawing" operation.

Other proposed distinctions are, for drawing, that the walls of the article should be "ironed", as in rod or tube drawing, and, for pressing, that the periphery of the blank should, as in the common Erichsen test, not flow inwards to any substantial extent. At present it must be accepted that in industry the terms "deep drawing", "drawing", and "pressing" are commonly used without proper distinction, except perhaps as regards the addition or omission of the prefix "deep".

No definition or distinction will be attempted in this paper, but the desirability that precise definition should be agreed upon, if possible internationally, hardly needs emphasizing, since at the present time the term "deep pressing", to give but one example, may conjure up two quite different press operations in the minds of different readers.

II.—LITERATURE.

It is often said that the art of deep drawing and pressing has received little scientific attention. A study of the literature shows, however, that many workers in many parts of the world have studied numerous separate facets of the main subject. An idea of the nature and extent of this work can be gained from the bibliographies prepared recently by the Iron and Steel Institute and the Institute of Metals,¹ the British Non-Ferrous Metals Research Association,² and, earlier, by the Institution of Automobile Engineers.³

The misconception that little scientific knowledge exists may have arisen owing to the fact that few serious attempts have been made to collect, sift, and apply to industrial practice the scientific knowledge available, and that unhappily the existing store is still woefully inadequate. This inadequacy is perhaps more evident in matters relating to the design of tools and apportionment of successive stages than in the more strictly metallurgical aspects of the art, although even here it must be admitted that what are commonly termed "deep-drawing properties" cannot yet be defined and measured in a precise manner.

III.—METHODS OF DEEP DRAWING AND PRESSING.

At first sight it might seem that the number of methods, or variations in technique, used in the craft of deep drawing and pressing to make sheet metal flow under press tools to form some desired shape is very

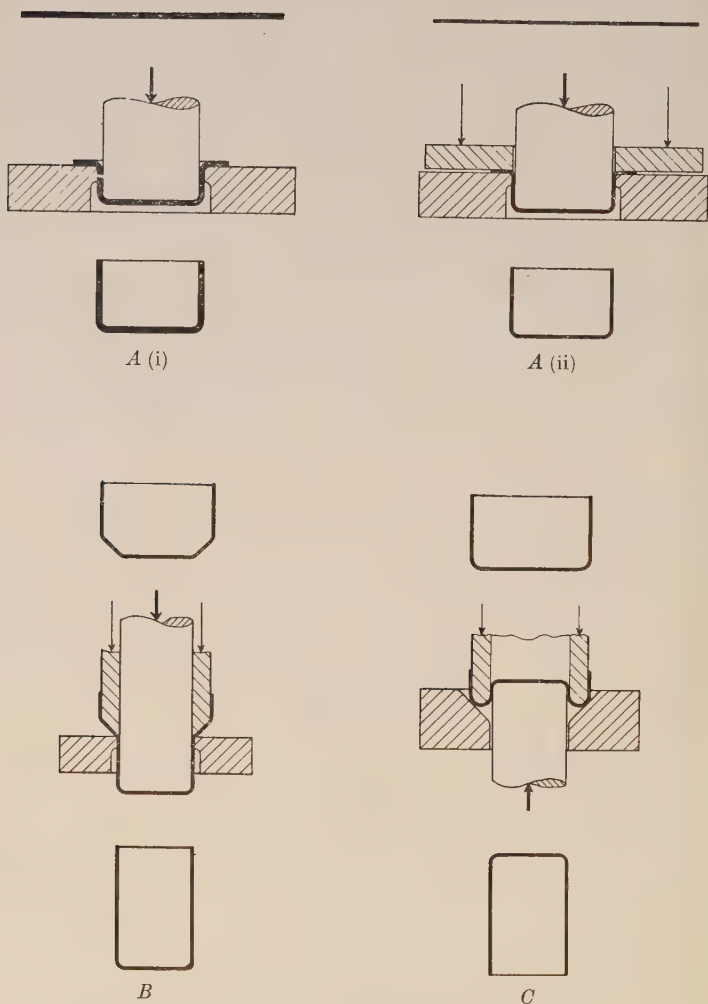


FIG. 1.—Diagrams Illustrating Various Methods of Deep Drawing and Pressing. For the sake of clarity the thickness of the sheet has been greatly exaggerated.

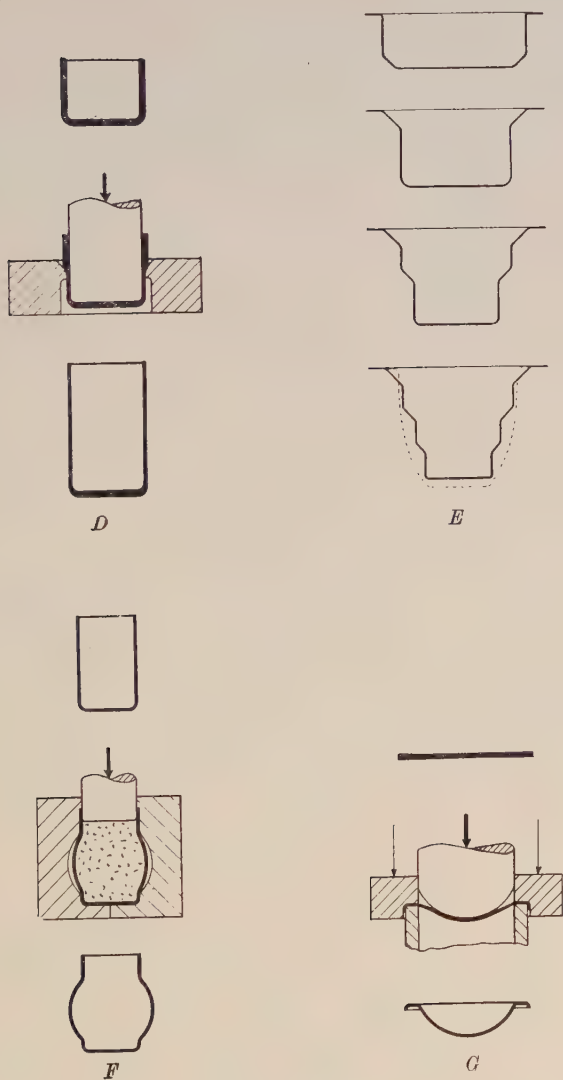


FIG. 1.—continued.

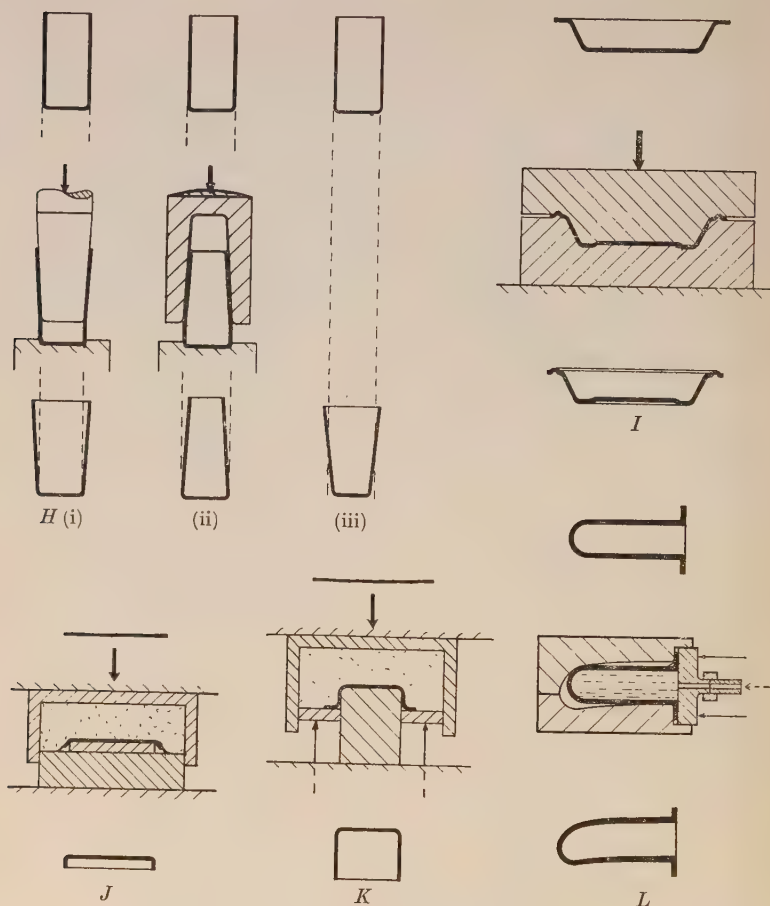


FIG. 1.—continued.

large. If these methods are studied, however, it will be seen that most of them are covered, at least in principle, by the five basic types of operation illustrated diagrammatically in Fig. 1 *A-E*. The large number of apparently dissimilar operations encountered in industry is explained by the common practice of combining two or more of these basic types to suit particular requirements, or sometimes the fancy of those whose task it is to design or to use press tools.

The first and simplest operation is that known industrially as "cupping" or "raising". In this a "cup" is formed from a flat blank, sometimes without a pressure-plate if the sheet is thick (Fig.

1 *A* (i)), but usually with the help of this adjunct to control the flow of the blank and to prevent wrinkling (Fig. 1 *A* (ii)). The pressure-plate may be actuated by the toggle mechanism of a double-action press, by an air cushion mounted on a single-action press, or indeed on a press of any type, or by a take-off from the main pressure system of an hydraulic press. It is common practice to use tools which both shear the blank from strip and then deep draw it at one stroke of a press. The combined operation is then known as "blank and raise".

When further deformation is needed the "cup" is redrawn one or more times with as many inter-stage annealing operations as experience shows to be necessary. There are four ways in which this is done, the basic principles of each being illustrated in Fig. 1 *B-E*. That most often employed is shown in *B*, the principle being that the diameter of the cup is reduced at each successive draw. A pressure-plate is generally used. When desired, a two-diameter stepped shell can be formed by limiting the travel of the punch.

A closely related method, termed "reverse drawing" (Fig. 1 *C*) is sometimes used, particularly for a second operation, i.e. a first re-drawing operation. In this method the cup produced by the first draw is turned inside out over the radiused end of a hollow die. It is generally acknowledged that, for reasons not yet understood fully, this change of direction enables a substantially deeper draw to be obtained before annealing becomes essential.

Fig. 1 *D* illustrates the third and least used method of redrawing, which differs from the other two in that instead of the diameter of the cup being reduced at each successive draw, as in *B* and *C*, the diameter remains substantially that of the original cup, depth being gained by "ironing" the wall by pulling it through a clearance space between punch and die which is less than the thickness of the wall as it enters this space. This method can give a shell having a base that is thicker than the walls, a combination which may or may not be welcome in any particular application. Ironing may be carried out in one heavy stage using a single die, or by passing the shell successively through several dies which give a comparable total reduction, an arrangement which enables more deformation to be accomplished before annealing becomes necessary. This is particularly so when the dies are arranged one below the other so that the shell, still on the same punch and heated up by its passage through the first die, is taken through the others while it remains hot.

Used in the ways just described ironing is intentional, but owing to various causes ironing sometimes occurs towards the end of ordinary draws of the kind shown in Fig. 1 *B*. Thus ironing may take place all

round the top part of the cup if the thickening is uniform or, should the sheet exhibit marked "directionality", only near the "troughs" of a badly "eared" cup where, as a result of reduced elongation in certain directions, the wall has thinned less than usual and therefore cannot pass freely through the normally adequate clearance space between punch and die. When this happens the extra tensile stress imposed on the wall of the drawn part of the cup may well cause failure. Sometimes a limited amount of ironing is imposed by design and not by accident in order to control the thickness of the upper part of the wall of a shell.

It may be desired to bulge out the parallel-sided walls of a deep-drawn cup to some convex shape. This is generally accomplished by using rubber compressed by the action of a solid punch, as illustrated in Fig. 1 *F*, to expand the shell into a hollow mould split to allow the bulged article to be removed. Fig. 2 (Plate LXIII) shows how this technique is used in the making of a salt-cellar. When the shape of an article renders the use of rubber impossible, wax is occasionally used in its place. The intense local deformation and pressure needed to form narrow beads, or ridges, such as the one seen in Fig. 15 (Plate LXVIII), leads to rapid disintegration of the rubber; hence, when the location of a groove enables it to be rolled in, this method is preferred. Where considerable numbers have to be produced of an article which for some reason, e.g. shortness of neck, is unsuitable for rubber bulging, an expensive multi-segment metal tool expanded by the action of wedges or other devices may have to be resorted to. If constriction instead of expansion is required, spinning is the preferred method when some contour, as distinct from a straight taper, is wanted.

The last method of redrawing, seldom used except for shells of conical or cigar-end form, consists of redrawing by method 1 *B* through a series of tools of different diameter to form a multi-stepped shell approximating to the desired shape, as illustrated in Fig. 1 *E*. The shell is then "coined" between suitable dies under a press or a drop stamp to obliterate the steps as far as possible and give the exact desired shape. In *E* the finished shape is indicated by the dotted line in the last multi-step shell.

To these five basic types of true drawing operation must be added at least seven other and less frequently used methods. Fig. 1 *G* illustrates a pure stretching operation having no accepted name, in which the periphery of the blank is held so that it cannot flow inwards and the whole of the required deformation is obtained by stretching, and consequent thinning, of the free area of the blank. This principle also holds in the "stretch-forming" of large components for aircraft.

When a straight taper is needed, punches and dies of the kind shown in Fig. 1 *H* are commonly used. In this way a parallel-sided shell may be expanded outwards (*H* (i)) or sunk inwards (*H* (ii)). Even when an annealed shell is used, not much expansion can be accomplished by method *H* (i) before the top of the shell splits. Rather more deformation can be achieved by sinking, method *H* (ii), but limits are imposed here by the tendency of the unsupported wall to fold or pucker during the early part of the stroke. The maximum possible amount of deformation can be attained by combining the two methods to expand the top and sink the bottom of a parallel-walled shell of near mean diameter, as shown in *H* (iii), where the diameter of the parallel-sided cup is indicated by a dotted line. The cocktail-shaker body illustrated in Fig. 3 (Plate LXIII) was tapered in this way.

The last basic type of press operation, illustrated in Fig. 1 *I*, is coining, a well-known operation in which a deep-drawn or pressed article, formed almost to finished shape, is squeezed between male and female dies mounted in a press or drop stamp. It is used to "sharpen up" existing details, particularly small radii, to give dimensional accuracy, to obliterate puckers or wrinkles, to form extra features such as grooves or dimples, or to impress some decorative pattern or other feature.

With the exception of rubber bulging, all the methods considered so far employ solid tools; but rubber, oil, and water are each used to force sheet into dies or on to formers. The general principle of rubber pressing, illustrated in Fig. 1 *J*, is that a large, and often laminated, block of rubber mounted in a steel container on the moving head of a large hydraulic press is used to apply pressure to blanks laid over formers resting on the stationary platen of the press. This method is only suitable for pressing shallow flanges or cups, because at the beginning of the stroke the rubber is compressed relatively lightly, and hence cannot exert sufficient pressure on the blank to prevent it wrinkling if proper deep drawing is attempted, even though, as is unusual, some form of pressure-plate is used. If this initial wrinkling could be avoided, the rubber technique offers several advantages for deep drawing and pressing. For example, it helps in the preservation of an initially good surface on the blank, it avoids all possibility of scoring and fouling during the drawing process, and for several reasons it appears to be capable of giving deeper draws than can be achieved when a solid punch is used. Considerable interest attaches, therefore, to a recent development, originating in America and known as the Marform process, which employs a pressure-plate actuated not by the rubber but by a separate hydraulic ram that enables any desired force to be applied to the pressure-plate before drawing begins and, a most im-

portant yet often overlooked advantage, to be varied in any desired manner as the draw proceeds. This arrangement is illustrated in Fig. 1 *K*.

The last method to be considered is that in which force is applied to the metal through the medium of air, water, or oil. Attempts to use air have nearly always proved unsatisfactory owing to the difficulty of making and maintaining an effectively sealed joint between the tools and the blank or cup. Oil and water are easier to control, but both are messy and invariably involve a rather slow cycle of operations. In spite of this, these media occasionally offer unique advantages for certain special bulging operations, or for forming curved or awkwardly shaped components such, for example, as are incorporated in some musical instruments. The principle of this technique is illustrated in Fig. 1 *L*.

All these methods have one object, namely, the production of the desired article in the fewest possible press operations with the fewest possible inter-stage anneals and with the least possible injury to the surface of the original sheet. Unhappily the attainment of this objective is often hindered by domestic limitations imposed by the number and the type of presses available, and sometimes by considerations of cost of material and even of the amount of discard from the blanking operation. Considerable ingenuity is often shown in overcoming hindrances and limitations of this kind.

The design of tools for deep drawing and pressing and the apportionment of successive stages is still carried out mainly by tool designers who rely almost entirely upon their own experience and make little use of the small amount of scientific data that exists. It is true that most power-press catalogues and some engineering reference books contain tables relating blank diameter to depth and diameter of cup, but these form no more than a very general guide to the production of the simplest cups under ideal conditions. Scientific study could provide welcome help here, particularly in the apportionment of successive draws which, experience shows, may need to be varied according to the particular metal or alloy being drawn.

Tool adjustment and setting, an item intended to include small changes in radii, easing of clearances, and similar minor alterations which practical trial in the press shows to be necessary or at least desirable, are often quite as important as matters concerning fundamental design. The adjustment of pressure-plate loading and the local easing of clearances to give the minimum restraint compatible with freedom from wrinkling is, in particular, a skilled and important task which nearly always has to be carried out with new tools. Similarly,

easing of the clearance space between punch and die in certain positions to accommodate local thickening, for example that which occurs in the vicinity of the corners in a shell of rectangular shape, may turn failure into success. Again the choice of lubricant, the quantity applied, and sometimes the position in which it is applied or omitted may reduce a very high scrap percentage, or even complete failure, to one of negligible proportions.

For these and other reasons it is likely that even though, as is to be hoped, scientific study gradually eliminates much of the guess-work and uncertainty now unavoidable, deep drawing and pressing will long remain a craft in which the skill and, let it be admitted, often intuitive knowledge of the craftsman will still count for much.

The choice of blank shape is a very important matter when the product is not of circular shape, the aim being to achieve as uniform an inflow of metal as possible and to avoid the local crowding or thinning so likely to cause failure. Hitherto the shape of the blank has been decided partly by guess-work concerning metal flow and partly by trial and error, for experiments with paper cut and folded to represent the finished article and then opened out are not very helpful for the obvious reason that although paper will bend, it is incapable of plastic flow. This drawback must apply in some degree to any inextensible substance, but a useful measure of success is claimed, particularly with pressings of irregular shape and contour, for the use of layers of cloth impregnated with some suitable substance, such as beeswax, to give it the necessary rigidity,⁴ and also of thermo-setting plastic sheet.⁵ With both these the technique is to squeeze a sheet between the appropriate tools, allow it to set, trim the edge, remove, and cause it to assume a flat shape, often in stages to represent consecutive draws. This method, which can also be used to study intermediate stages, appears to be particularly useful in the case of irregular pressings for aircraft, for example, exhaust manifolds.

IV.—PRESSES.

Although any extensive discussion of presses is beyond the scope of this essentially metallurgical paper, two matters, the application of hydraulic methods of punch actuation and of mechanically actuated multi-punch presses, call for some consideration because both have an important bearing on the behaviour of sheet during deep-drawing and pressing operations.

1. *Methods of Press Actuation.*

The moving heads of presses used for deep drawing and pressing are nearly always actuated in one of three ways: by rack and pinion, by

hydraulic pressure, or by crank. Of these the rack and pinion is rarely seen, and its use is confined to very deep draws, for example, bicycle-inflator tubes or shell cases. At present hydraulic pressure is employed only on a small proportion of the total number of presses in operation in industry, the majority being actuated by the familiar crank, which is simple, cheap, durable, easily maintained by non-specialist engineers and, together with its near relation the cam, seems at present to be the only possible method when high speeds are demanded.

Having regard to its desirable features, it is therefore calamitous that of the three methods of press actuation just cited the crank is by far the worst when judged by its "kindness" to the sheet being deep drawn or pressed. Indeed, were it desired to shape sheet metal in a manner calculated to produce the *least* amount of useful deformation before fracture, the crank would closely follow the iniquitous drop-stamp. Only custom and continued familiarity with crank actuation can have led to uncomplaining acceptance of the unwelcome harmonic motion which it imparts to the moving head and to the consequent brutal impact of the punch when, as happens often, it strikes the metal while travelling near the maximum of its continually changing velocity. Moreover, the speed—in whatever sense this word is applied to a crank press—cannot be varied easily and quickly nor, indeed, over a wide range.

The hydraulic press, on the other hand, offers two most valuable features, namely, a speed which remains constant throughout the stroke, and the means whereby this speed can be quickly adjusted to any value between zero and maximum. Two minor but useful advantages are the availability of an instantly adjustable loading of the pressure-plate, and the continuous indication, on separate gauges, of the pressure being applied to the moving head and to the pressure-plate. Another welcome feature is the reliable functioning of a pre-set release valve which prevents the press from being overloaded, whereas the all too frequent breakage of frames and cranks bears costly testimony to the unreliability of the several forms of mechanical safety device commonly incorporated in the transmission systems of crank presses.

Both crank and hydraulic presses have had, and indeed still have, their protagonists. It is, therefore, of interest and significance to observe that the continued insistence on the advantage of the hydraulic press by those having a scientific outlook is being confirmed by the practical man on the floor of the shop. This is seen most clearly in shops where both types of press are installed, for there it will be found that, once the inherent conservatism of setters and superintendents has been overcome, the more "difficult" draws will inevitably be allocated

to the hydraulic presses. Indeed, when a particular draw is giving a high percentage of scrap on a crank press, its transference to an hydraulic press, without any modification to the tools, often results in a trouble-free run.

In view of the advantages just described it is therefore unfortunate that the substitution of hydraulic presses for crank presses is seriously hindered by three factors: their high first cost, their unsuitability for high operating speeds, and the need for specialized engineering skill and knowledge to maintain them. Of these the first could doubtless be reduced if sufficient numbers were made. Operating speeds have already been increased substantially and may well be raised still more. Maintenance may, unhappily, still remain a problem in shops insufficiently large to carry a specialist engineer.

2. *Multi-Punch Presses.*

When several operations are needed to shape an article, handling (meaning transport between, and individual insertion in, each successive press) represents a significant proportion of the total cost of production. It is therefore surprising that far more extensive use is not made of continuous multi-punch presses in which work is automatically carried through up to six, eight, or even ten sets of tools, or so-called "stations", by mechanical slides or fingers. Presses of this kind give excellent service in, for example, the making of small-arms ammunition cases and caps for electric-lamp bulbs and tubes. When, as in the instance of the cap illustrated in Fig. 4 (Plate LXIII), no inter-stage annealing is needed, it often happens that strip is fed automatically into one end of the press and completely finished articles emerge from the other end untouched by hand.

Valuable but not immediately apparent advantages are that work has no opportunity to become damaged or to pick up dirt during handling between successive press operations; that lubricant is applied automatically at each stage and not according to the fancy of several operators and by means of possibly dirty rags; and, lastly, that all draws after the first are carried out on warm metal, a benefit which though as yet unconfirmed by scientific study has a weight of practical experience to substantiate it.

Another important advantage is that very often a greater number of stages can be used to form a given shape and that in consequence the treatment accorded to the metal can, in press-shop parlance, be "kinder". When a separate press is used for each operation it is obviously important to inflict the utmost amount of deformation at each stage in order that as few presses as possible need be allocated

to any one job and that handling costs may be reduced. When a multi-punch press is used it often happens that more than enough stations are available, and hence a bigger safety margin can be allowed at each operation to accommodate sheet of slightly sub-standard quality. For this reason, an article which needed an intermediate anneal when formed on separate presses can sometimes be made on a multi-punch press without this unwelcome and sometimes hazardous operation, so upsetting to the continuous line-flow which delights the heart of the modern production engineer.

When to these benefits is added the saving in floor space and the very great saving in initial cost between a battery of, say, eight separate presses and one eight-station multi-punch press, the small use made of the last-mentioned type is indeed surprising.

V.—TOOL MATERIALS.

It is sometimes stated or implied that, compared with those used for steel sheet, less care need be exercised in the selection, heat-treatment, finishing, and even maintenance of the tools used to deep draw and press non-ferrous metals. This belief is incorrect, and it is certain that, through encouraging complacency, it has caused much unnecessary trouble. It is true that both pressure and abrasion tend to be less than with steel; but non-ferrous metals score far more readily, and often have a greater tendency to "load" or "foul" the die. Because of this, and because in many instances it is even more necessary than with steel to reduce frictional drag to as low a value as possible, it is more important to give, and to maintain, a really good polish to the working surfaces of the tools used to deep draw and press non-ferrous sheet. This is no idle statement. The standard of finish tolerated on many tools used for steel simply will not do for many non-ferrous metals, in particular aluminium.

Materials commonly used to make tools for deep drawing and pressing non-ferrous sheet are tungsten carbide, carbon and alloy steels, cast iron, zinc alloy, rubber, and wood.

1. *Sintered Carbides.*

When used for dies, sintered carbide gives many times the life of the best carbon or alloy steel no matter how treated. Furthermore, when properly maintained and lubricated it imparts a remarkably smooth surface to the metal drawn through it. From most aspects it is the best tool material yet available, and only its high cost, particularly when dies are of large size, hinders its extensive application.

At first sight it might seem that the use of a carbide die could be

economic only when a very large number of one article, which otherwise would need many replacement steel dies, had to be produced. In fact, a combination of less obvious advantages often justifies its adoption when longevity alone would not. The excellence of surface imparted to the drawn product has already been mentioned. This can be so good that polishing costs can often be reduced very substantially and, when a mirror surface is not imperative, the polishing needed when steel tools are used can sometimes be eliminated altogether. Deeper draws can nearly always be obtained owing to reduced friction and to smoothness of surface, thus enabling the number of press operations to be reduced. Any tendency to "load" or to "foul" is lessened. Lastly, much closer dimensional limits can be maintained over long periods than is possible with steel dies. When limits of size are close this may render the usual final "sizing" operation unnecessary, thus releasing a press for other use. It will be appreciated that these benefits may make a carbide die preferable, and indeed truly economic, even when the life given by a low-cost steel die is adequate.

To obtain the best results from sintered-carbide dies special methods must be used to polish them, they must be carefully maintained, and if breakage, an expensive matter, is to be avoided, proper backing and support must be provided. These aspects are dealt with in detail in literature relating to the subject.

2. Carbon Steels.

Plain carbon steel is used very widely in non-ferrous press shops because it is cheap, easy to obtain and to harden, and gives entirely adequate service in many instances.

Carbon steels for punches and dies usually fall into one of three classes containing, respectively, about 0.7, 0.9, and 1.2% carbon. Normal methods of hardening will give a hardness of C62-63 Rockwell; but, by the use of pack-hardening, values as high as C65-66 can be obtained, a condition much sought after on small dies used on long-production runs. Choice of carbon content will depend upon what the tool has to do and, a point not always appreciated, upon its size and shape. Serious hardening hazards are sometimes caused by the selection, through ignorance or carelessness, of steel having an unnecessarily high carbon content. This is particularly so with punches, because these have to withstand much less abrasion than dies, and the higher ranges of carbon are seldom necessary.

Case-hardened mild steel is used occasionally when pressures are low. Heavy draws, and particularly ironing, will cause the case to "cave in" and crack owing to the inability of the core to withstand the

resultant high compressive stress, a happening often attributed quite incorrectly to bad heat-treatment.

3. *Alloy Steels.*

Alloy die steels consist mainly of two types, namely, tungsten and high-carbon high-chromium varieties. The first, which may contain from 1 to 6% tungsten, sometimes with a little chromium, gives a slightly higher hardness than plain carbon steel of the same carbon content. It is used mainly for small, high-output dies, and is often pack-hardened to give a value in the region of C66 Rockwell. The second, containing from 1.2 to 2.4% carbon with 12-14% chromium, is a most useful variety having as its principal feature very good wear-resistance. As it is oil-hardening, the hardening hazard for large or awkwardly shaped tools is much less than with the carbon or carbon-tungsten steels. It is important that the free carbides in this type of steel be dispersed by adequate hot working. If this has not been done, the presence of stringers or colonies of carbide particles will prevent a really good polish being obtained and will greatly increase the difficulty and cost of polishing.

Steel of the ball-race type, containing about 1% carbon with 1-1.5% chromium, offers a fair measure of wear-resistance, but it is not a popular die steel.

Medium-carbon oil-hardening alloy steels containing chromium, sometimes with nickel, are used occasionally for punches, but their wear-resistance is generally too low for dies.

4. *Nitrided Steel.*

Although of proved benefit in many instances in preventing both wear and "loading", the nitriding of steel tools is not a popular practice. Reasons for this may be that special steels are needed and that, except in large organizations which have their own nitriding equipment, tools which are probably urgently wanted have to be sent away for a period of some days to be nitrided.

Both the aluminium and the chrome-molybdenum type of nitriding steel are used. The first gives a surface hardness of over 1000 V.P.N. and should be chosen in preference to the other (700-800 V.P.N.), whenever its rather pronounced brittleness and fragility on corners can be tolerated. With either type of steel it is important that the grade which gives the highest tensile strength, usually in the region of 100 tons/in.², be used to prevent the very hard nitrided case from "caving in". The use of steels of lower "core" strength has been responsible for failures which in not a few instances have led to a hasty and un-

warranted general condemnation of nitrided tools. When, as happens sometimes, even the 100-ton tensile grades of the usual nitriding steels have an inadequate core strength, nitrided high-carbon high-chromium steel often offers an effective solution with, if anything, the benefit of still greater wear-resistance. It is unfortunate that the nitriding properties of this steel are not more widely known for, in the opinion of the author, nitrided high-carbon high-chromium steel gives the best wear-resistance of any tool material yet available with the single exception of sintered carbides, a much superior but very costly alternative.

5. *Chromium Plating.*

The benefit of chromium plating on tools is still a matter of controversy, even though on the evidence available it seems tolerably certain that, when deposited properly, hard chromium is of real value in most instances. It possesses an inherent "slippery" nature, thus reducing friction, and, provided that it is deposited on a really smooth underlying surface, reduces any tendency toward scoring. It also reduces the liability of bare steel tools to "foul" or to "load", this being perhaps its most useful property under the majority of industrial conditions. On the other hand, failures attributable to unsatisfactory electro-deposition, although not always recognized as such, have been so numerous that some press shops have given up chromium plating as a welcome, but as yet industrially unreliable, help.

By varying the conditions of deposition the hardness of chromium can be varied over a substantial range, but at present the influence of the hardness of the chromium deposit itself, as distinct from that of its steel base, upon its behaviour in the press shop is an almost unexplored field. The usefulness of the so-called "porous" or "crazed" chromium deposit, which in theory seems to offer valuable lubricant-retaining properties, has yet to be established under working conditions.

Opinions differ as to the best hardness for the underlying steel. From the service aspect the harder this is the better, and the wider the field of application before the chromium deposit "caves in". It has been the experience of some users, however, that the harder the steel base the greater the danger of premature failure of the deposited chromium layer. For this reason some recommend a maximum hardness of C55 Rockwell, or possibly of only C50 Rockwell, a value which restricts the application of chromium-plated tools to comparatively light operations devoid of ironing. In other cases no trouble is met with when the hardness of the underlying steel is as high as C62

Rockwell. The explanation of these conflicting experiences probably lies in the nature of the preparatory cleaning treatment given to the hard steel and, perhaps to a less extent, in the method of plating and in the chemical analysis of the steel. The difficulty of plating increases with both the carbon and the chromium content; hence, as the wear-resistance of the steel itself is no longer of significance, a steel free from chromium, and of the lowest carbon content which will give the desired hardness, should be used as a base for deposited chromium.

Heating tools to a temperature of about 150° C. immediately after plating is often advocated, but the various reasons given for this, for example relief of stress, relief of hydrogen embrittlement, and diffusion of the chromium into the surface of the steel, show that the purpose of this treatment is not yet understood.

6. *Cast Iron.*

Cast iron is deservedly popular as a tool material. It is cheap, easy to machine and polish, and resists scoring and "loading" more than most tool materials. It has the advantage that it can be cast approximately to shape, and this practice is, indeed, always advisable in order that the working surfaces of a die may be near the original surface of the casting and thus as sound and of as fine a structure as possible.

The varieties of cast iron used for tools for deep drawing and pressing are quite numerous. Depending upon the kind of sheet involved, upon operating conditions, and upon length of run, ordinary grey iron and alloy iron, both as cast and heat-treated, acicular iron, and in a few instances chilled iron, find application. It is fair to say, however, that many press shops still fail to take advantage of the low cost and very useful performance of dies made from the better grades of cast iron which have become available during recent years.

The unique, so-called "self-lubricating" properties of cast iron, which are one of its most valuable features as a die material, are commonly attributed to the influence of the graphite flakes embodied in its microstructure. The truth of this assumption may well be questioned, however, for it seems very unlikely that the limited number of graphite flakes exposed at the surface of the radius and throat of a drawing die will survive the severe abrasive action of tens and even hundreds of thousands of severe draws. The fact that no diminution of "self-lubricating" properties occurs as the period of life increases suggests that it is the porous, lubricant-holding nature of cast iron rather than the presence of graphite which is the true explanation of its welcome behaviour.

7. *Zinc Alloy.*

During the last war the use of zinc alloy tools became popular in the aircraft industry. Since then their application has extended very considerably, and their popularity is still increasing.

The outstanding feature of zinc alloy press tools is that they can be cast to size from a suitable prototype or pattern and need very little finishing. As a result both the cost and the delivery period of zinc tools is but a fraction of those of steel, or even of cast iron, tools, particularly those of medium and large size. When from the performance aspect zinc is satisfactory but for some reason the casting process cannot be used, it may still be preferable to machine from a solid block of zinc, because this metal can be machined many times as rapidly as steel or cast iron.

At first it was thought that the life of zinc tools would be so short that they would prove useful only for prototypes or for very short production runs with aluminium or other soft sheet. Experience has shown, however, that even when used for dies as distinct from punches, zinc alloy often has a surprisingly long life. In consequence it is being used more and more for production runs of substantial duration when the loading on the radius and throat of the die is not unduly high.

The zinc alloy commonly used is a proprietary one containing small proportions of aluminium, copper, and magnesium, which has a hardness in the cast condition of about 80–100 Brinell compared with about 40 Brinell for pure zinc. The technique employed for moulding and casting has been described repeatedly in the technical Press, but for the benefit of those who may be unfamiliar with the process it may be said that when making a pair of press tools it is common practice to cast the die first in a sand or plaster mould and then to use the die as a mould in which the punch is cast. The same alloy is often used for the punch, but sometimes an alloy of lower melting point, such as antimonial lead, is used to lessen the danger of fusion with the die during the casting operation.

Tools machined from slabs of rolled zinc usually have a surprisingly long life when used for blanking. Worn or obsolete zinc tools have a high scrap value, for they can be melted down and the metal used over and over again. Many large press shops now have a zinc foundry and pattern shop in, or attached to, them.

8. *Rubber.*

Relatively little information has been published concerning rubber itself, as distinct from the method of using it in the press shop. As a rule little thought is given to the choice of rubber for bulging operations,

but in the technique known as rubber pressing, in which a large rubber bolster is used, the hardness of the rubber, measured on the Shore durometer, is often varied between 40 and 70 according to the work in hand. To facilitate proper vulcanization, large bolsters are often built up from separate sheets of rubber.

9. *Wood.*

The use of wood, sometimes in its natural state but more often impregnated with some substance such as synthetic resin to harden and strengthen it, and to give dimensional stability under atmospheric changes, is restricted almost entirely to the stretch-forming of panels, mainly in light alloy, for aircraft. For this purpose it has adequate life and, when kept free from foreign particles, does not score. Wood faced with case-hardened mild steel, "rule steel", or even cold-rolled mild steel, is used occasionally for blanking and light drawing operations on light alloys.

Maple and yellow or red (but not white) birch are said to possess a high compressive stress in a direction parallel with the grain.

VI.—LUBRICANTS.

Having regard to the very important part which lubricants play in the successful achievement of almost every deep-drawing or pressing operation, the lack of scientific study, the paucity of informative published matter, and the meagre knowledge which exists among those not in the drawing-lubricant industry is deplorable. Those who wish for more information than can be given in this short review are referred to the work of Halls,⁶ to previous discussion by the present author⁷ and, more recently, by Murphy,⁸ Cairns,⁹ Johnston,¹⁰ Bastian,¹¹ and by Evans, Silman, and Swift¹²; but all these, and others cited by them, deal only with the subject in general and often vague terms.

One reason why it is difficult to compile a short review of lubricants used in the press shop is that a very large number of different kinds of lubricant are used. Thus Bastian¹¹ has listed no less than fifteen general types, a lengthy classification which cannot be considered here. A more simple but necessarily incomplete grouping would comprise four general types: (i) straight mineral oils, (ii) fatty and compounded oils, (iii) solutions or emulsions of soluble oil or soaps, and (iv) the so-called "drawing compounds" or pastes.

Straight mineral oils of varying viscosity find wide application in many kinds of press operation on all kinds of non-ferrous metals and alloys, being easy to apply and to remove and adequate for many purposes. Oils of fairly low viscosity are generally used, but occasionally a quite viscous oil is preferred. For example, a thick oil has been

found to be far more effective than a thin one in preventing the formation of small yet troublesome score marks on the inside of deep-drawn aluminium articles caused by the movement of the sheet over the punch.

The second group, fatty and compounded oils, covers a very wide field, having as its main features a film strength higher than that of straight mineral oils, ease of application and, generally, ease of removal. It includes both straight fatty oils such as lard, sperm, and rape oils, and also compounded oils, that is a mixture of fatty oils with mineral oil. To any of these, small amounts of various substances may be added to increase the film strength still further, to enhance wetting power or, sometimes, to prevent spreading. Oils containing sulphur, particularly when in the free form, which is the more efficient, tend to cause unsightly yet, unless the action is prolonged, often harmless staining on many non-ferrous metals and alloys. In the particular instance of nickel and high-nickel alloys they may cause serious injury unless completely removed before pressings are annealed. Lubricants containing sulphur or chlorinated additives should always be removed from work as soon as possible.

Lubricants of the third type, solutions and emulsions of soluble oils and soaps in water, are as popular as oil in many non-ferrous press shops, and are easy to apply and to remove. Extensive use is made of "suds", the name given to water-base lubricants containing a proportion of soluble or emulsifying oils or soaps. Suds are commonly thought of as an easily removable but not very efficient lubricant suitable only for light draws. In fact, much depends upon the nature and quality of the additions made to it. Thus suds containing good-quality soap, lard oil, or wool fat, used in moderately concentrated form, and even with sulphur or chlorinated additives, will often prove entirely satisfactory for draws well beyond the capabilities of what is often understood by the term "suds", that is, a very dilute solution containing ingredients of poor quality or of a kind which do not give a high film strength.

The last group, drawing compounds, covers a wide range of lubricants usually of proprietary origin and of complicated and undisclosed composition. Proprietary compounds are nearly always purchased in the form of a thick paste which, although sometimes applied neat for very severe draws, is generally broken down with oil or water to meet particular requirements. They usually contain soaps, mineral oils, and fatty oils, often with a solid, inert "filler". The purpose of the filler, commonly chalk or whiting, is to assist in preventing metal-to-metal contact by purely mechanical separation and to hinder the true lubricant with which it is mixed being squeezed out.

These can be regarded as basic ingredients, and it is in the choice and proportions of these, and in the nature and amount of other small, and often chemically active, additives in which compounds differ.

Graphite is occasionally added to both oil and drawing compounds. It is a quite outstandingly efficient lubricant, but because it is very difficult to remove is not widely used. Deodorants and substances claimed to prevent operators contracting dermatitis are sometimes incorporated in proprietary oils and compounds.

Once a lubricant has accomplished its task of preventing metal-to-metal contact between sheet and tools during a deep-drawing or pressing operation its presence becomes undesirable, and even harmful, instead of beneficial. Unhappily, the efficiency of a lubricant as regards its main function nearly always varies inversely as its ease of removal. Thus the solid matter in "filled" lubricants can seldom be removed without recourse to high-pressure sprays or mechanical rubbing; and chemically active lubricants, for example those containing calcium oleate, sulphur, or chlorinated additives, cannot be entirely removed by trichlorethylene vapour or by ordinary alkali rinses.

Much trouble could be avoided if, when a lubricant is being chosen, the problem of its subsequent removal were always kept in mind. Indeed, the influence of this matter often extends further; for, if special facilities for the removal of strongly adherent lubricants are not available, the tools and apportionment of draws used to produce a given article may have to be designed or altered to ensure that easily removed, and hence less efficient, lubricants will be adequate from all aspects.

VII.—INTER-STAGE ANNEALING.

Although the modern tendency is to curtail, and whenever possible to eliminate, the inter-stage annealing of deep-drawn or pressed parts, in many press shops dealing with non-ferrous metals and alloys annealing is likely to remain for some time an unwelcome yet unavoidable process. To the metallurgist it seems strange that annealing has always proved such a stumbling block to those who shape sheet metal. Not many years ago the sheet supplier's dictum that the user would ruin any metal if he annealed it was substantially true. Even to-day it must be admitted that, particularly among those small firms who still use batch-type annealing furnaces, often of considerable age and very varying temperature distribution, incorrect annealing is responsible for more trouble than all other processes put together.

Although the present tendency is to use continuous conveyor furnaces whenever the amount of work justifies their cost, many shops still rely on batch-type furnaces, and it is encouraging to observe that,

particularly on those which work at a relatively low temperature, the use of fans to circulate the atmosphere is becoming more common. The most uniform heating of all is provided by furnaces in which air is circulated continuously at high velocity over heating elements and through the charge, and it is unfortunate that the high cost of this type in relation to the size of its working chamber has tended to hinder its use for the inter-stage annealing of pressings.

Both gas and electricity are used for heating. The choice of electricity is usual when protective atmospheres derived from ammonia are employed; but although when partially burnt town's gas is adopted for a protective atmosphere it seems logical to use gas for heating, this cheap, and often adequate, atmosphere is also used in electrically heated furnaces.

Roller hearths and wire-mattress conveyor belts both have their advocates. Owing to the relatively low temperatures employed, the life of belts is substantially longer with non-ferrous pressings than with steel.

In large shops the use of continuous conveyor furnaces employing various kinds of protective atmosphere has become almost general except for aluminium and aluminium alloy pressings, which do not need a protective atmosphere. During the early industrial application of protective atmospheres the term "bright annealing" was coined and, seeing the admirable results obtained with steel, many believed that the true bright annealing of all non-ferrous pressings would soon be possible. Although a great deal of effort has been put into attempts to achieve this end it must be admitted that little real progress has been made towards bright annealing those alloys which contain a substantial proportion of zinc. This is particularly disappointing in view of the fact that brass forms the bulk of the sheet used in most non-ferrous press shops. The gradual replacement of "bright annealing" by the more accurate term "clean annealing" seems to be a tacit admission of failure. This does not mean that "clean annealing" is of little value. On the contrary, the surface condition given by clean annealing is sufficiently good for many purposes. When a truly bright surface is desired it can be obtained easily by giving clean-annealed pressings a quick dip in some suitable pickling solution.

A truly bright condition can be approached with nickel, cupronickel, and nickel silver, but it is a chastening thought that, in the opinion of many, best results are still given in the case of copper by the intelligent use of water-sealed conveyor furnaces of the kind in use long before the industrial advent of special, and far more costly, protective atmospheres.

It is not possible in this paper to consider in detail the individual peculiarities and requirements of non-ferrous metals as regards protective atmospheres. A concise yet informative review of these has recently been made by Hancock.¹³ More detailed information is available in a book by Jenkins¹⁴ devoted to the subject, and in the papers presented at a symposium held under the auspices of the American Society for Metals.¹⁵

The most common causes of unsatisfactory clean annealing are incorrect atmosphere control; overloading, either by over-filling or by increasing the speed of the belt in a misguided attempt to exceed the rated capacity of a furnace; and, last and by far the most common, failure to remove drawing lubricant from the pressings put into the furnace. It is truly remarkable how many expensive and efficient clean-annealing furnaces never really justify their cost or upkeep solely owing to this one cause. The fact that, unlike the viscous, heavily-filled drawing compounds used on steel, the lubricants used in non-ferrous press shops can usually be removed simply by rinsing in suitable solutions renders their non-removal still less excusable.

It is important that all work be cooled below tarnishing temperature before it emerges into the atmosphere. Forgetfulness of this seemingly obvious precaution sometimes leads to much needless work being done in attempts to put right a protective atmosphere which is, in fact, perfectly satisfactory. Information concerning approximate tarnishing temperatures is available.⁷

Whether or not a protective atmosphere is used, it is surprising how much incorrect annealing arises, even to-day, from the complete and unimaginative faith which those in charge of the operation often have in pyrometers. They forget, or fail to realize, that the mere fact that the extremity of a pyrometer fitted to a furnace happens to indicate some specified temperature is no guarantee whatever that each and every, or indeed any, pressing in that furnace has reached or will reach the indicated temperature. It is hardly too much to say that a pyrometer can sometimes convey a sense of entirely unwarranted safety and complacency even to those who know what it does and what it does not do. Mass, time, closeness of packing, method of heating, temperature variation over the hearth, and other factors must always be taken into account.

VIII.—CRITICAL-STRAIN CRYSTAL GROWTH.

A trouble for which those responsible for annealing are sometimes unjustly blamed is surface roughness, and even failure, caused by the incidence of critical-strain crystal growth during the inter-stage anneal-

ing of pressings made from those metals and alloys susceptible to this troublesome phenomenon. In fact, there is little that the annealer can do except to see that the rate of heating is rapid and the time of soaking short. When pushed to an extreme these conditions give what is termed flash-annealing. In this process work travels at a relatively fast rate through a furnace zone maintained at a temperature substantially higher than that which it is desired to reach, being prevented from reaching furnace temperature solely by the short time it is held within the hot zone. This method is giving good results with aluminium sheet or cut blanks, but its application to pressings as distinct from flat sheet, particularly to those of moderate or large size, presents a problem, because even when forced circulation is used it is difficult to heat all parts of each pressing to the same temperature for the same time when this time is short.

In the non-ferrous field aluminium and its alloys give most trouble; hence every possible effort should be made to form the desired shape without the help of inter-stage annealing or, if this is unavoidable, to ensure that all parts of a deep-drawn or pressed article have been given a fairly heavy amount of deformation. Critical-strain crystal growth has been observed in copper, brass, nickel silver, and aluminium bronze, but, fortunately, trouble due to this is seldom encountered in the industrial press shop. A useful summary of information dealing with recrystallization and grain growth has been prepared by Baker.¹⁶

IX.—PICKLING.

The pickling of pressings is an even more unwelcome ancillary operation than annealing. During the last war considerable interest was aroused by the introduction of self-contained, enclosed spray-pickling units through which brass shell cases passed on a conveyor belt, thus avoiding nearly all the unpleasantness inseparable from the dipping and transference of pressings along a series of open vats. This method has not been widely adopted, however, probably because the increasing popularity of clean-annealing furnaces has reduced pickling to a quick dip. It may also be that firms whose limited output or capital prevents them from installing a costly clean-annealing furnace cannot for the same reason afford a spray-pickling plant.

X.—PROPERTIES OF SHEET DETERMINING ITS BEHAVIOUR DURING DEEP DRAWING AND PRESSING.

In the Introduction to this paper it was said that the exact properties, or combination of properties, responsible for the behaviour of sheet under the press were not fully understood.

This admission may cause surprise, but those metallurgists who work in close collaboration with the press shop are forced to acknowledge that attempts to use the commonly measured mechanical properties and metallographic observations to predict the behaviour of sheet under the press are often far from successful. By this it is not meant that the common tests and observations are useless. On the contrary, they serve a useful purpose in revealing sheet of undeniably unsatisfactory quality; but it often happens that of two consignments of sheet adjudged satisfactory and apparently similar by usual metallurgical standards one will behave well and the other badly.

A fact which increases the difficulty of correlation, and one which is not sufficiently recognized, is that different kinds of press operation call for different properties in the sheet used. A good illustration of this is provided by the deep drawing of a simple cylindrical cup in commercially pure aluminium, using orthodox tools and pressure-plate. Under these conditions if the cup has a hemispherical bottom a deeper draw is obtainable with fully annealed sheet, but if it has a flat bottom $\frac{1}{4}$ -hard, or even $\frac{1}{2}$ -hard, sheet will give the better performance.

The same metal offers a striking example of the failure of ordinary mechanical tests to predict deep-drawing qualities. It is commonly believed that a high percentage elongation value in the tensile test is desirable, and even essential, in sheet having good deep-drawing properties, and that a low Erichsen value is indicative of poor behaviour. Yet in the case of pure aluminium a far deeper draw can be obtained under many conditions, for instance under those just described, if $\frac{1}{4}$ -hard, or sometimes $\frac{1}{2}$ -hard, sheet is used instead of fully annealed sheet, even though its percentage elongation and its Erichsen value are far below those given by the annealed sheet. To add further confusion, in the deep drawing of magnesium-aluminium alloy into automobile body panels it is found that the opposite obtains, for here a very light amount of cold rolling seriously impairs the deep-drawing properties of the sheet.

Setting aside tensile and other commonly used values for the moment, a little thought will show that what is needed in most deep-drawing and pressing operations is sheet which will work-harden to an extent and at a rate that will enable two things to happen simultaneously. First, the walls of the deep-drawn article must become and remain able to transmit adequate stress to the undrawn part of the blank beyond the radius of the die without fracturing, or indeed thinning unduly, under tension. Secondly, the undrawn part of the blank must be able to continue to change shape by decreasing in diameter under the action of combined stresses without work-hardening to such an extent that the

stress needed to make this portion flow rises beyond that which the wall of the article below the die radius can transmit. The satisfactory manner in which many metals achieve this apparently difficult and delicate compromise between what may be described in general terms as "tenacity" and "ductility" is both welcome and remarkable.

It must be accepted that at present there are no reliable measurements by which the deep-drawing and pressing properties of sheet may be assessed, a matter considered in more detail in Section XI, where the testing of sheet is discussed. When, therefore, some metal or alloy is said to have good deep-drawing properties it is implied that practical experience, and not precise measurement of certain values, has shown this to be so. For the same reason comparison is most difficult because indefinite terms such as "good" or "fair" have perforce to be used instead of numerical values.

Passing from properties of a mechanical or physical nature, there are a number of features, some desirable and others undesirable, which have an important bearing upon the behaviour of all kinds of sheet when deep drawn or pressed. Of these, crystal structure is one of the most important. A large crystal size will give a rough surface on the drawn article coupled with good ductility; but, if too large, the wall of the article will tend to fracture before the whole of the blank has been drawn in. A small crystal size gives a smooth surface, but lower ductility will limit the amount of "flow". Only experience can determine the crystal size which provides the best compromise for any particular article and sheet. An adjudged "average grain-size" of about 0.030–0.040 mm. is useful for many applications, but not infrequently values both above and below this are preferable, and even necessary.

It is most important that the size of all the crystals should approach as closely as possible that of the adjudged average. An aggregate containing a few very large crystals will tend to give a rougher surface than that expected from its "average" size, and the presence of a considerable proportion of very small crystals will seriously impair the ductility or "flowing power" of the sheet. During recent years sheet suppliers have gone some way towards giving users the average grain-size for which they ask or, when they do not ask, they need, but serious lapses are still encountered with nearly all non-ferrous metals and alloys. Uniformity of size often leaves much to be desired.

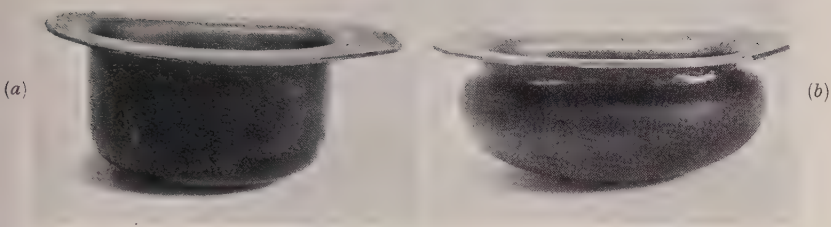
Anisotropy, or as it is called industrially "directionality", is nearly always unwelcome, but can occasionally be used to advantage in pressings not of circular shape when the discard from the blanks is not rendered excessive by a choice of orientation not based on economy.

When pronounced, anisotropy causes premature breakage in the press because the flowing power of the metal in certain directions is reduced substantially. This same effect leads to the formation of "ears" at the periphery of a drawn cup, which if marked may cause the troughs of the wavy lip to extend below the trimming line of the finished article. In non-ferrous metals and alloys anisotropy is usually attributable almost entirely to effects associated with the crystal structure; but when, as in light alloys of the Duralumin type or in α -brass containing β , particles of another constituent occur in the form of stringers, these too exert an influence.

It has been known for some time that the severity, and often the orientation relative to the direction of final rolling, of the "directionality" exhibited by sheet could be controlled by varying the sequence of reductions and anneals given to sheet in the mill. During the past few years a considerable amount of work has been done to ascertain the effect of these variables, for example by Cook,¹⁷ Cook and Richards,^{18, 19, 20} and Wilson and Brick²¹ on copper and brass; by Bassett and Bradley²² on nickel silver; and by Chevigny²³ and Spillett²⁴ on aluminium. Enough is now known to enable the makers of non-ferrous sheet to give users sheet in which directionality, if not entirely absent, is never sufficiently pronounced to cause serious trouble. It is the users' hope that this knowledge will be applied more and more.

Surface defects such as the old familiar "spills" are, happily, far less common than they used to be, owing to the fairly general adoption of so-called "scalping" operations in which the cast surface is machined completely away at the beginning of or during the rolling sequence. This improvement in surface has tended to focus attention on mechanical defects caused by handling and, when "clean annealing" is not used, on defects having their origin in annealing or pickling.

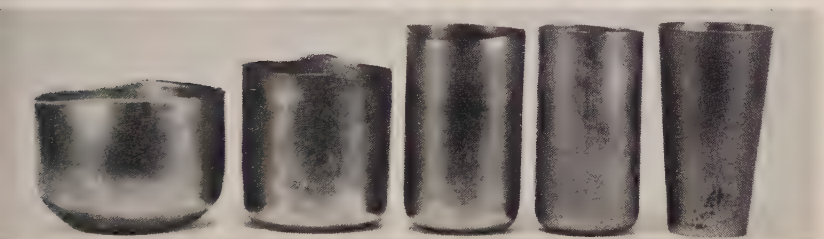
Surface smoothness is a feature concerning which it is difficult to generalize. For very many years the user wished for, and the supplier tried to give, sheet having as near a mirror finish as possible. When as a result of continual improvement in plant and methods the desired end began to be approached, it was discovered that from the particular aspect of deep drawing and pressing a very smooth shiny surface was not always as favourable as had been expected. Reasons given were that the very smooth surface failed to "hold" drawing lubricant, and that the sheet was difficult to control and in consequence tended to be erratic in its method of in-drawing and flow. A very finely matt surface is therefore preferred by many users, notably on brass and nickel silver, for much aluminium and aluminium alloy sheet is supplied with something approaching a mirror finish.



[By courtesy of Walker & Hall, Ltd.]

FIG. 2 (a).—Deep-Drawn Nickel Silver Cup.

(b).—Cup Bulged with Rubber to Form Salt-Cellar Body. Approx. $\frac{2}{3}$ natural size.



[By courtesy of Adie Bros., Ltd.]

FIG. 3.—Production of a Cocktail Shaker in Nickel Silver in Four Draws and Only One Tapering Operation, with Annealing.



[By courtesy of Lamp Presscaps, Ltd.]

FIG. 4.—Stages in Production of a Brass Lamp Cap on a Multi-Punch Automatic Press.

[To face p. 590.]

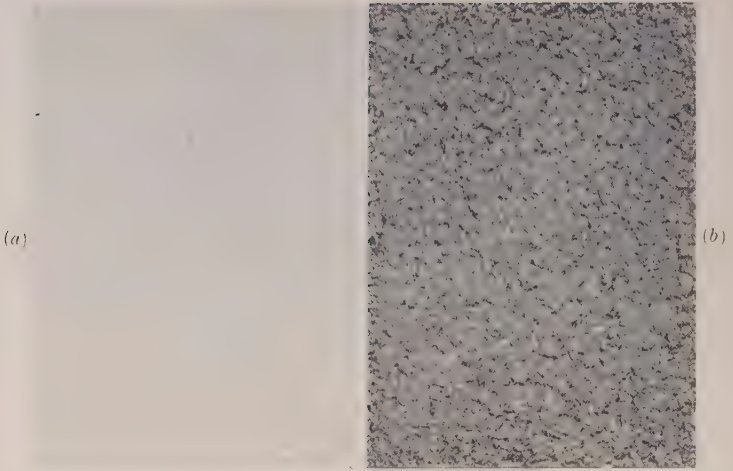
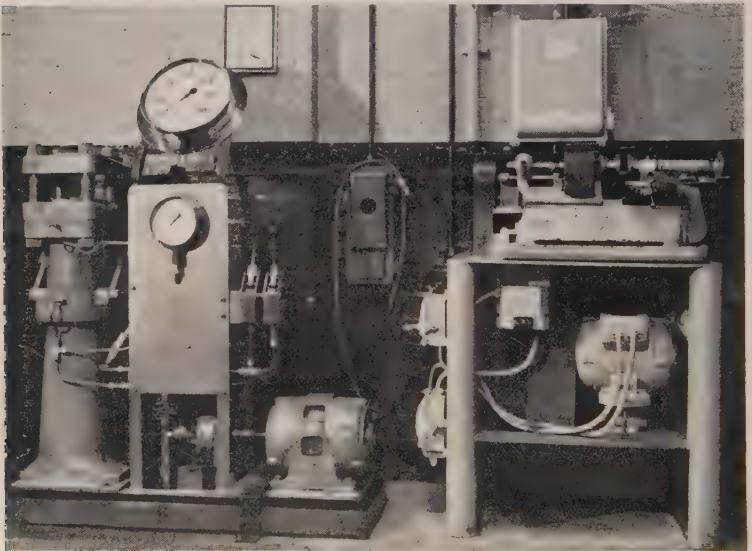


FIG. 5 (a).—Appearance of Surface of Polished 63 : 37 Brass Blank. $\times 5$.
(b).—Appearance of Surface of Flat Bottom of Cup Deep Drawn from this Blank. $\times 5$.



[By courtesy of Joseph Lucas, Ltd.]

FIG. 6.—Apparatus for Determining Maximum Size of Blank which can be Deep Drawn into a 2-in.-dia. Standard Cup.

(Left) "Swift" hydraulic cupping press fitted with special high-delivery oil pump and open-scale pressure gauge.

(Right) Lathe adapted for rapid machining of blanks of various diameters from sheet.

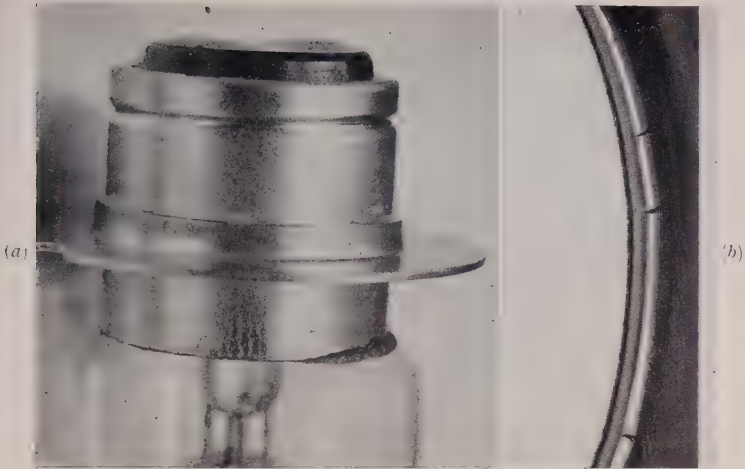


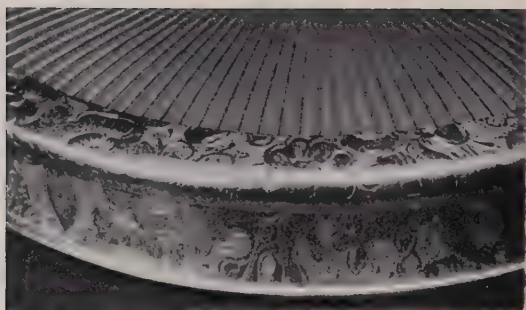
FIG. 7 (a).—Season-Cracking in Deep-Drawn Brass Bulb Cap.
(b).—Season-Cracking in Deep-Drawn and Rim-Rolled Nickel Silver Flange. Approx. $\times 1\frac{1}{2}$.



[By courtesy of The Pressed Steel Co., Ltd.]

FIG. 8.—Appearance of Stretcher-Strain Markings in Aluminium-Magnesium Alloy Sheet. Approx. $\times 1$.

(a) Flamboyant wedge type of marking on automobile door panel. Unetched.
(b) Parallel-band type of marking on tensile test-piece.



[By courtesy of Hill Bros. (Birmingham), Ltd.

FIG. 9.—View of Wall of Powder Compact Deep Drawn from Pre-Patterned Brass Sheet and Rubber Bulged to Form Protruding Corner Radius.

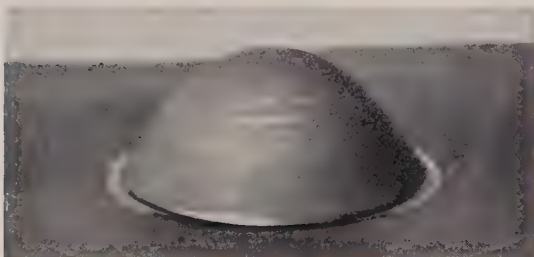
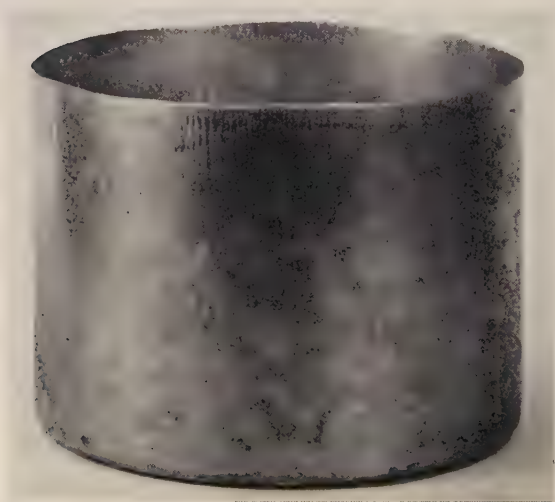
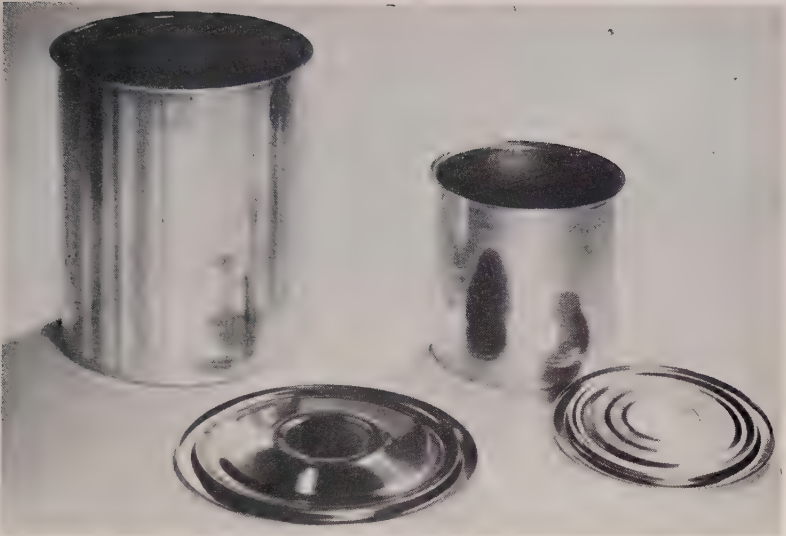


FIG. 10.—Appearance of Erichsen Dome in "Gassed" Copper Sheet.



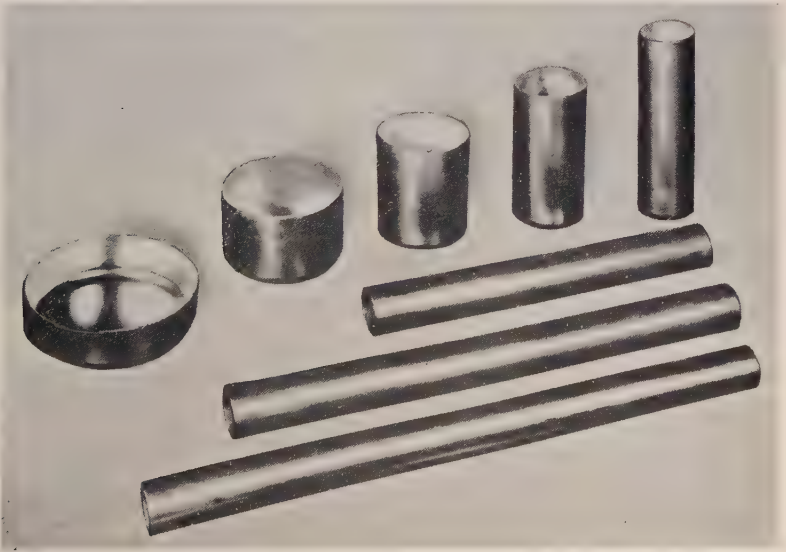
[By courtesy of The Mint (Birmingham), Ltd.

FIG. 11.—6-in.-dia. Copper Shell Deep Drawn in One Operation to a Depth of $4\frac{1}{2}$ in.



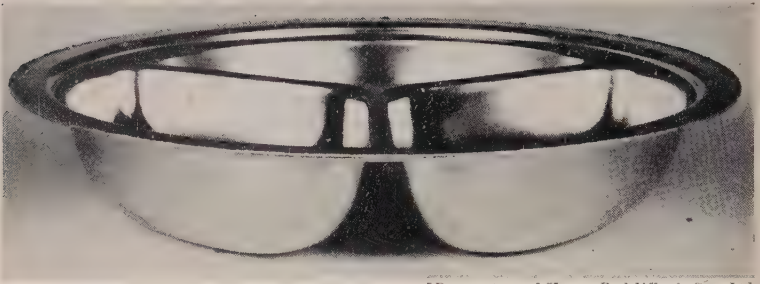
[By courtesy of Aluminium Laboratories, Ltd.]

FIG. 12.—Food Cans Deep Drawn from Pure Aluminium Using an “Ironing” Technique.



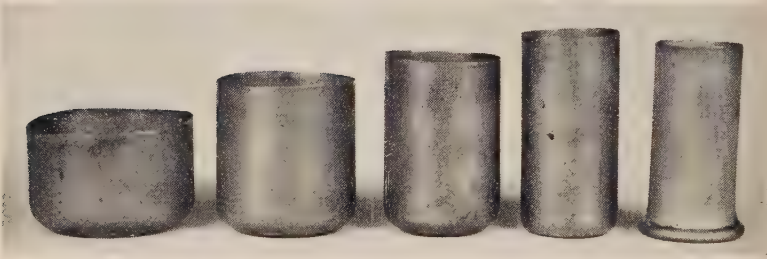
[By courtesy of Mallory Metallurgical Products, Ltd.]

FIG. 13.—A 1-in.-dia. Tube Deep Drawn in Eight Stages, with Annealing, from a 7-in.-dia., 0.090-in.-thick Blank of Copper-Beryllium-Cobalt Alloy.



[By courtesy of Henry Radcliffe & Co., Ltd.]

FIG. 14.—Three-Compartment Vegetable Dish, approx. 10 in. in dia., in Nickel Silver Deep Drawn almost to the Depth Shown in One Draw and then “Sharpened Up” by a Second Operation.



[By courtesy of Adie Bros., Ltd.]

FIG. 15.—Stages in the Deep Drawing of a Pepper-Pot $\frac{7}{8}$ in. in dia. from a Blank of Sterling Silver $3\frac{1}{4}$ in. in dia. and 0.014 in. thick. The bulge at the base is formed with the aid of rubber.

If, on the other hand, some sacrifice in ease of deep drawing is accepted, the possibility of starting with sheet having a polished surface and of preserving this carefully during deep-drawing or pressing operations has occurred to many, and plastic films have been tried as a surface protection, particularly on aluminium. Those who advocate this technique usually forget that the kind of plastic deformation suffered during deep drawing or pressing will itself roughen a polished surface owing to the partial rotation of crystals, or perhaps of blocks of crystals, in the structure of the sheet. For this reason, although some measure of success is possible, realization of the full desired aim cannot be achieved.

The limitations of this technique are illustrated by the two photographs shown in Fig. 5 (Plate LXIV), which were both taken at 5 magnifications and under the same conditions of illumination. Fig. 5 (*a*) shows the surface of a pre-polished 63 : 37 brass blank of approximately 0.035 mm. "average grain-size". That on the right shows the surface of the flat bottom of a cup deep drawn from this blank in the Swift cupping press. It will be seen that the mirror finish of the blank has changed to a coarse matt as a result solely of the movement of the crystals, for this part of the blank has not touched the die.

Troubles attributable to the influence of internal discontinuities and segregation of planes of non-metallic inclusions, so common in steel, seldom arise with non-ferrous sheet. On the other hand, those who use non-ferrous strip in progressive tools complain that deviation from straightness is a constant source of trouble and one which seriously restricts the length of tool which can be employed, and that less variation in thickness and in width would be welcome.

XI.—TESTING OF SHEET METAL.

Elsewhere in this paper it is stated that the ordinary methods by which metals are tested and examined in the laboratory seldom provide the basis for a reliable prediction of the deep-drawing and pressing properties of sheet. Although this is true, some of the common tests do enable sheet of unquestionably unsatisfactory quality to be detected. Furthermore, by a judicious combination of these tests qualified observers can make a useful, if not infallible, forecast of behaviour in the press shop, particularly when a background of experience in the making of any particular product exists. It will therefore not be idle to discuss some of these ordinary tests from the aspect of deep drawing and pressing, and to consider in what respect they fail in their desired object. Lastly, some of the special tests devised in an attempt to measure quantitatively the elusive combination of properties which determine

how sheet behaves when it is deep drawn and pressed will be examined.

Laboratory tests which yield information concerning deep-drawing and pressing properties can be divided into three groups :

(1) Tests commonly applied to metal for other purposes, e.g. hardness and tensile tests, bend tests, chemical analysis, metallographic examination, and X-ray examination.

(2) Special tests which do not attempt to imitate the action of a punch and die, e.g. tear-length, wedge-drawing, magnetic, and special tensile tests.

(3) Special tests intended to simulate the actual deep-drawing or pressing process. These fall into two classes : the popular "cupping" tests and the less popular true deep-drawing tests. Both of these make use of a die and pressure-plate and deform the sheet either by a solid punch or by hydraulic pressure.

1. *Common Tests.*

(a) *Hardness Tests.*

Of the common tests, the measurement of hardness is the simplest and most easily carried out. It can, therefore, be performed on a large number of samples, thus enabling a relatively high percentage exploration to be made of incoming coils or lengths of strip. For these reasons it is widely used even though it gives no real information concerning deep-drawing and pressing properties. Its usefulness lies in the fact that sheet having a hardness substantially higher than the value which experience has shown to be normal for its particular kind, can safely be rejected without further examination, thus saving much time and money in the press shop. On the other hand, compliance with the normal hardness value is no guarantee whatever that sheet will behave in the desired manner under the press, a fact which production personnel often have difficulty in understanding.

Because speed is the only virtue of hardness tests in the special application under consideration, routine tests are usually made on Rockwell machines and not on the much slower though scientifically preferable Vickers machines.

(b) *Tensile Tests.*

It is becoming recognized that, particularly when considered in the light of experience, the results of the ordinary tensile test offer a more useful guide to the probable behaviour of sheet under the press than was formerly believed.

Of the properties commonly measured, percentage elongation is often the most informative; although it is likely that percentage

reduction of area would take prior place if its accurate measurement on specimens cut from thin sheet were easier.

It is not widely enough recognized that the percentage elongation measured on a gauge-length of 8 in. is often much more discriminating than that measured on a specimen having a 2-in. gauge-length. The reason for this is that the elongation or "necking" which takes place just before fracture has less influence on the total elongation value of an 8-in. than of a 2-in. test-piece, and that in almost all deep-drawing and pressing operations it is the behaviour of the sheet within the plastic range before local necking—the incidence of which is tantamount to failure—that is important.

Some metallurgists carry this idea further and use what is often termed the "general elongation" value. This is the percentage elongation measured on 6 in. of an 8-in. gauge-length, the 2 in. including and adjacent to the fracture being neglected. As this is probably the most informative method of any for measuring elongation in the tensile test, its very limited industrial, or indeed academic, use is regrettable.

In the case of steel sheet many workers in the automobile-body pressing industry attach considerable importance to the yield point: maximum stress ratio exhibited by any samples of sheet, and consider that a large interval between these two values is indicative of good behaviour under the press, particularly when a pressure-plate is used. In spite of the fact that most non-ferrous metals lack a well-defined yield point, there seems no reason why more attention should not be directed to some ratio of this kind which, determined as it is by the capacity of sheet to undergo work-hardening, is a most important one.

From both the industrial and the academic aspect the information given by reasonably accurate stress/strain curves is most valuable, and it is unfortunate that the time needed to obtain the necessary readings restricts their use in industry. Curves obtained by autographic recording methods are frequently on too small a scale to enable possibly important differences to be revealed with certainty.

(c) *Bend Tests.*

Whatever the metal, sheet of deep-drawing quality will withstand the usual 180° flat bend test which, useful for revealing internal "lamination" in steel sheet, is of little value when applied to non-ferrous sheet. Two special bend tests deserve mention, however. In one, made on a machine known as the Tour-Marshall bend tester,²⁵ it is claimed that an accurate stress/strain curve can be obtained more quickly than in the tensile test. In the other, devised by Thompson,²⁶ it is claimed that the use of a tapered specimen bent between special

tools enables the ductility, as well as the minimum bend radius, of a specimen to be evaluated in a precise manner. Although intended primarily for sheet which has to be bent, it is possible that this simple and rapid test might be of some use in the examination of sheet intended for deep drawing and pressing.

(d) *Metallographic Examination.*

This can be a valuable help to those whose task it is to predict the behaviour of sheet. The feature most commonly observed is crystal size, but regularity of size as distinct from the adjudged average size should always be studied. Purists rightly question both the meaning and the significance of the popular term "average crystal size", meaning a value obtained by inspection, or even by precise measurement, carried out on a microspecimen prepared in the usual way.²⁷⁻³⁰ Although this criticism is justified, the fact remains that the *appearance* of the crystal structure when viewed at a standard magnification, and when necessary compared with standard photomicrographs or charts, does yield helpful information to experienced observers.

Other features which should always be noted are the size and distribution of inclusions; the nature and disposition of a second phase when one exists; evidence of chemical segregation, often seen best when a specimen is viewed slightly out of focus; and, lastly, any special features associated with particular metals and alloys, such as the presence and distribution of β constituent in supposedly α brass.

(e) *Chemical Analysis.*

As a rule this can only yield information of a general nature, but its usefulness in special instances will be obvious. Even the estimation of harmful impurities can be misleading, because local segregation in sheet having an apparently satisfactory impurity content, estimated, as it must be, as an average value, may lead to widespread failure under the press. On the other hand, sheet relatively high in some impurity, which is, however, well disseminated, may give no serious trouble.

(f) *X-Ray Examination.*

The slowness and costliness of this method restricts its use to research work. Its main application for the particular purpose under consideration is to gain information concerning anisotropy in the crystal structure, but even here it supplements rather than supplants information derived from mechanical tests. Its usefulness in determining crystal size is limited, but it is of value in studying the effect both of cold work and of annealing on crystal structure.

2. *Special Tests (Not Imitative).*(a) *Tear-Length Test.*

This quickly-made test is claimed to give an indication of the degree of anisotropy present in sheet and, by some, even of "average crystal size". It is made by tearing out a tongue of metal in a direction parallel with and another at right angles to that of rolling, and sometimes in other directions, and comparing their length. In the original form of the test as devised by Brownsdon this was done by making two parallel saw cuts 1 cm. apart and pulling the flap with pliers. The present author has obtained more uniform results by using a slotted rod to wind a tongue out smoothly.⁷

It is hard to say exactly what this test measures. Differences in tear length in different directions in any given sample of sheet are, clearly, caused by anisotropy; but quantitative agreement between these differences and behaviour under the press is often disappointing. In fully annealed sheet the tear-length value in any given direction can be used to provide an indication of approximate "average crystal size" by reference to a previously determined relationship for sheet of exactly similar chemical composition.

(b) *Special Tensile Tests.*

In the opinion of some investigators "true" stress/strain curves give a better indication of deep-drawing properties than do the usual or "nominal" curves. By "true" curves are meant those in which increments of strain are plotted against stress per unit area of test-piece calculated not, as is the usual procedure, on the area of the test-piece at the start of the test, but on the true sectional area measured at each increment of strain. It is claimed that true stress/strain curves give a better picture of behaviour in the plastic range than do ordinary curves. On the other hand, it can be argued that the part in which they show the most difference from ordinary curves lies beyond the onset of necking, a condition which should not be reached in good deep-drawing practice. Be this as it may, making "true" stress/strain curves is far too slow a procedure to be used in ordinary acceptance testing and, in the instance of thin sheet specimens, is particularly difficult.

Norris,³¹ Sommer,³² and others have proposed various forms of derived stress/strain curves purporting to give a clearer picture of special features, such as rate of work-strengthening, which are of importance. At present these have mainly academic interest, but they offer a fruitful field for study and practical application.

Lankford, Snyder, and Bauscher³³ claim that excellent prediction of behaviour in the press shop can be made if what they term the

"*R* value" is considered in conjunction with the "*n* value". The *R* value is the ratio of the reduction in width to the reduction in thickness sustained by tensile specimens cut in one or more chosen directions from the sheet to be tested, and the *n* value is obtained from the equation:

$$\text{True Stress} = k (\text{True Strain})^n$$

derived from a true stress/strain curve taken on the same sheet, *k* being the strength coefficient and *n* the strain-hardening exponent. They state that, although correlation with behaviour is then not quite so good, the yield point: ultimate strength ratio can be used in place of *n*, thus eliminating the true stress/strain curve and enabling all the necessary information to be gathered from one relatively quick tensile test.

(c) *Wedge-Drawing Tests.*

This test, devised in its original form by Sachs,³⁴ has for its main object the imposition of compressive stresses at right angles to, and simultaneously with, the main unidirectional axial stress normally applied to a tensile specimen, thus imitating to some extent the conditions which obtain during many press operations. This is accomplished by pulling a wedge-shaped tensile specimen through a die or chamber having sides at the same taper and a clearance space approximately equal to the original thickness of the sheet to be tested. The ratio of width of top of taper to length of taper on a standard specimen at the greatest width of specimen which can just be drawn through the die is termed the "deformation number", and is used as a basis for comparison.

This ingenious test has been tried by many workers, and a number of modifications, mostly aimed at reducing the friction at the tapered edges, have been proposed. Some claim that it gives a better indication of deep-drawing and pressing properties than do ordinary tensile or cupping tests, but others, including Swift,³⁵ the last to study this test, have failed to find reliable correlation. It is possible that if, as happens sometimes with the ordinary tensile test, its results were considered in the light of long industrial experience, it would prove to be not less informative, and probably more discriminating, than the tensile test.

Kayseler³⁶ has used the wedge-drawing procedure as the first operation in a two-stage test. This investigator draws a relatively large specimen to a predetermined extent and then makes miniature Erichsen impressions at different positions along the originally tapered, but now parallel, part of the test-piece. Curves are plotted relating depth of cup to the average elongation undergone by the wedge at the position of each cup. It is claimed that this combined test is more

discriminating than either the wedge-draw test or the Erichsen test used singly.

3. *Special Tests (Imitative).*

(a) *Cupping Tests.*

The principle on which all the common cupping tests are based is that a piece of sheet is gripped between rings and the free central portion is gradually forced into the shape of a dome or cup until fracture occurs, the depth of the cup at the point of fracture being taken as the basis for comparison. In some kinds of cupping test, as in the Erichsen, which is the most popular of all, the sheet is not gripped really tightly but is allowed to flow inwards under some restraint. In others, particularly when the dome is formed by means of hydraulic pressure instead of by a solid round-nosed punch, the rings grip the specimen so tightly that the sheet is prevented from being drawn inwards at all and a pure "bulging" or bursting test, as distinct from a true "drawing" test, is imposed. Other forms of this test in which a parallel-sided cup is deep drawn will be considered later under the heading of "true deep-drawing tests" in order to distinguish them from the bulging tests which by long use of the term have, rightly or wrongly, come to be known as cupping tests.

The simplest, quickest, and most widely used of the cupping tests, the Erichsen, is too well known to warrant description here. The claim that it enables the deep-drawing and pressing properties of sheet to be predicted has been widely criticized, and even its advocates have to admit that, not unexpectedly, the forecast which it gives is more reliable in the instance of press operations which in principle resemble the Erichsen test than in those where true deep drawing is done.

The Erichsen test has certain other inherent disadvantages. For example, the Erichsen value varies, on metal having identical properties, according to the thickness of the sheet; hence, as with the gauge-length in a tensile test, the thickness should always be stated. Moreover, experience shows that the thinner the sheet the less reliable is the information given. Again, different operators usually obtain slightly different results on any given machine—a particularly unfortunate fault.

Notwithstanding these failings the Erichsen test provides certain indirect information which is of considerable, and often unappreciated, value in enabling the quality of sheet to be judged and its probable behaviour in any press operation to be predicted to a useful, albeit limited, extent in the light of experience. Neglecting therefore the significance of the Erichsen (depth of cup) value itself, the roughness of the dome is a good indication, first, of the "average crystal size" of

the sheet and, secondly, of the surface texture to be expected on any particular deep-drawn or pressed article. From the type of fracture, i.e. whether circular, straight-lined in one direction, or straight-lined in two directions at 90° to one another, useful conclusions can be drawn concerning the nature and degree of "directional" properties exhibited by the sample. Lastly, in those metals which are prone to stretcher-strain markings, the absence or severity of these markings on the flat surround of an Erichsen specimen drawn not quite to fracture furnishes a useful indication of the susceptibility of any sample to this defect.

Information on these three or four matters alone, coupled with the ability of the depth of cup measurement to reveal sheet of genuinely poor quality, renders the test of real value in most instances, particularly having regard to the fact that, unlike lengthier and more complicated tests, it can be made on a large number of samples by almost unskilled labour. Recognition of the fact that the Erichsen value itself cannot always be correlated directly with behaviour under the press is sensible, and indeed overdue. Discontinuance of this once popular test on account of this failing, and without regard to its other uses, is foolish.

The Avery cupping test resembles the Erichsen except that the clamping rings are reversible and that both are serrated on one face. It is claimed that the difference between depth-of-cup measurements obtained using the smooth faces of the rings with 0.05 mm. clearance as in the Erichsen test, and the serrated faces clamped tightly constitutes a more discriminating test than either method used singly. Owing, perhaps, to the longer time needed to carry out this test, it has never achieved the popularity of the ordinary Erichsen.

The Olsen and Amsler machines resemble the Erichsen, but use a draw-, or die-, ring of 50 mm. dia. instead of 27 mm. dia. as in the Erichsen, the punch being 20 mm. dia. in all three instances.

The Guillery test, another variation, is similar to the Erichsen except that force is applied to the punch by a piston actuated by hydraulic pressure instead of by a screw. A more precise end-point is claimed, and the machine will deal with sheet of greater thickness.

Owing probably to a certain unavoidable messiness, hydraulic cupping or bulging tests are unpopular. The best known is the Jovignot, used on the Continent. In this country, the so-called N.P.L. machine was devised by Gough and Hankins;³⁷ but, as far as the author is aware, it is not used industrially. Hydraulic tests have the advantage that with the help of pressure and depth gauges a stress/strain curve can be plotted autographically which of necessity applies to the weakest direction in the specimen and not, as in an ordinary tensile test, to the direction in which the specimen has been cut.

The K.W.I. test, developed by Siebel and Pomp at the Kaiser Wilhelm Institut, might be more correctly described as an expanding rather than as a cupping test. A machine resembling an Erichsen is used, but the punch, instead of being hemispherical, is flat-bottomed with a central circular projection which fits into a central circular hole in a square test-specimen. This arrangement enables a flat-bottomed cup to be drawn, the end-point of the test being the appearance of radial cracks at the edge of the hole in the base and the value measured being the depth of cup. It is claimed to be more discriminating than the usual forms of cupping test. Esser and Arend³⁸ have used a test which though similar can be carried out more quickly.

(b) *Deep-Drawing Tests.*

This group comprises those tests in which a genuine draw is carried out on a laboratory-type press using punch, die, and usually blank-holder. Tools for doing this on a standard Erichsen machine are marketed, but it is more customary to employ a specially designed miniature press. Some of these, such as the A.E.G., are actuated by means of a screw, but for several reasons hydraulic actuation of both punch and pressure-plate is convenient and preferable. A number of individual investigators, e.g. Swift,³⁹ have designed and constructed their own hydraulic presses, and a press based on Swift's design is now made in this country. One of these, installed in the laboratories of Joseph Lucas, Ltd., and illustrated in Fig. 6 (Plate LXIV), embodies modifications which include a more sensitive pressure gauge, an automatic pressure-depth recorder, and a pump capable of giving punch speeds up to 36 in./min., instead of the 12 in./min. previously available.

Opinions differ as to what should form the basis of measurement and comparison in true deep-drawing tests of the kind under consideration. At present the preferred value seems to be the maximum diameter of blank which can be drawn without fracture under stated, though as yet unstandardized, conditions. The adoption of this particular value has the disadvantage that for every sample tested several blanks have to be machined accurately to different sizes, a somewhat slow procedure. It seems, therefore, that tests of this kind must at present be regarded as being more appropriate to research than to the everyday acceptance testing of sheet under industrial conditions.

Although it might be expected that so-called true deep-drawing tests would offer many welcome advantages, much remains to be done before useful and reliable results can be obtained consistently and, of importance, before sheet suppliers will agree to a test of this nature being made the main feature of routine acceptance testing. Not the

least of the difficulties to be overcome lies in the fact that present experience suggests that a punch and die of some standard size and shape, a condition which would be very desirable if any test is to gain universal acceptance, would have only limited usefulness; for in order to reveal the finer differences which are of such importance the shape of the tools used to test the sample would have to correspond, at least in type if not accurately as regards scale, with those under which the sheet was to be shaped in the press shop. In other words, it would be unwise to use a hemispherical-ended punch to test sheet which in the shops was to be drawn over a flat-bottomed punch, or to use a round cup to test sheet destined to be drawn into a rectangular box having corners of relatively small radius. It is possible that a fair indication of behaviour in many circumstances might be given by a minimum of three quickly changeable sets of tools based on a round hemispherical punch and a round flat-bottomed punch utilizing a common die, and a rectangular flat-bottomed punch with its appropriate die. Unfortunately, the complication and the opportunities for confusion of results, were this scheme to be employed for the routine testing of hundreds of sample a day by a supplier having many customers, detracts from its possible value.

Further difficulties which have to be faced are the standardization of lubricant, of speed of drawing, and of the type and method of use of pressure-plate; for all these influence the results obtained.

From what has been said it will be clear that there seems little hope that any simple, generally applicable, laboratory test of the kind so desired by industrialists will shortly become available. It may be that progress will be made both in the development and in the application of special forms of tensile test devised to yield information concerning both capacity for plastic deformation and capacity for and rate of work-hardening, although anisotropy in samples must never be forgotten. On the other hand, it may be found that more or less empirical true deep-drawing tests using miniature tools give a better prediction than precise scientific values having fundamental significance.

At present, the routine examination of sheet destined for the press shop must, perforce, be based on a few easily carried out tests selected from the substantial number available. Which and how many of these are to be applied, and to what proportion of samples, will depend on how much a user deems it wise to spend upon the testing of incoming sheet. In the opinion of the author, a useful compromise for the industrial testing of sheet lies in the regular application of the following four tests, made in the order given and on a decreasing proportion of

samples : hardness, Erichsen, metallographic examination, and tensile tests. Although the purpose and limitations of each of these tests have already been discussed in some detail, it is perhaps desirable to indicate very briefly the more important functions of each of the chosen four in the proposed scheme.

The hardness test often eliminates sheet of unquestionably unsatisfactory quality right at the outset, and gives an indication of *probability* that a group of samples, particularly when they are from the same consignment, are, or are not, similar. The Erichsen test gives visible evidence of the practical effect of, first, the degree of anisotropy present in the sample and, second, the crystal size and related causes of surface roughness resulting from deep pressing. The appearance of the microstructure furnishes experienced observers with a very useful, though admittedly by no means infallible, guide to the behaviour to be expected under the press. Tensile tests are included because, more than any other common laboratory test, they measure fundamental properties and because their results, like those of metallographic examination, can be used by men of experience to predict probable behaviour under the press.

It should be observed that of these four tests the first two, hardness and Erichsen, can be carried out quickly on large numbers of samples by relatively unskilled and inexperienced assistants; that the information yielded is instantly applicable to many kinds of sheet, processes, and products; and furthermore that the results are not worth preserving for study, correlation, and future reference. On the other hand, the last two, metallographic examination and tensile tests, are by comparison lengthy, and hence can be applied only to a much smaller number of samples. They require assistants possessed of a certain amount of skill for their efficient carrying out and a not inconsiderable amount of experience for their proper and useful interpretation in collaboration with the press shop; their results should always be preserved. It follows that the information afforded by metallographic examination and tensile tests are more useful when a background of experience has been built up with some particular kind of sheet, process, and product as a result of regular examination over a substantial period. In such circumstances these two tests will sometimes enable a tolerably reliable prediction of behaviour to be made by observers who are familiar with all the relevant facts.

XII.—SEASON-CRACKING.

Because many products of non-ferrous press shops are liable to fail by season-cracking, no review of deep drawing and pressing would be

complete without at least a brief mention of this annoying phenomenon. No theoretical discussion will be attempted. Those interested in this aspect are referred to the excellent review of present knowledge by Chaston,⁴⁰ to the relevant papers in the symposium held by the American Society for Testing Materials and the American Institute of Mining and Metallurgical Engineers on the stress-corrosion cracking of metals,⁴¹ to a survey by Stettler,⁴² to previous discussion by the present author,⁷ and to the many references cited in these works.

As regards the industrial aspect, it is well known that season-cracking is most virulent in alloys which contain a substantial proportion of zinc, notably in brass. It is often stated that brasses containing less than 20% of zinc are virtually immune; but, although it is true that susceptibility increases with increasing zinc content, there is ample evidence to show that low-zinc brasses do sometimes fail. Season-cracking occurs in nickel silver and, among the zinc-free alloys, to a limited extent in aluminium bronze and silicon bronze. It is known to be caused by the action of trace substances in the atmosphere, notably of ammonia or amines in the presence, it is now believed, of moisture and carbon dioxide.

Industrially the belief persists that the tendency to season-crack increases with the amount of plastic deformation inflicted. This is not so. It is the magnitude of the residual or unbalanced stresses which determines whether an article will or will not season-crack. Indeed it often happens that heavily worked metal is in a less dangerous condition than lightly deformed metal, or that further deformation, for example that caused by rolling a lip or ridge on the periphery of a deep-drawn cup, may cause a substantial reduction in the tendency of an article to fail by season-cracking.

As for the practical aspect, although both its cause and the simple means for its prevention are widely known, season-cracking is still responsible for a certain proportion of failures among deep-drawn or pressed articles. Unless the article is stressed in service, these failures can nearly always be traced either to the deliberate or unintentional omission of a final low-temperature stress-relieving anneal, or else to the fact that annealed pressings have not reached the proper temperature, for reasons explained elsewhere in this paper, even when this temperature is shown on the furnace pyrometer. Typical examples of season-cracking in brass and in nickel silver are shown in Fig. 7 (Plate LXV).

The well-known mercurous nitrate test still offers the most convenient means for revealing the presence of what are likely to prove dangerously high residual stresses in brass; but it must be admitted that the correlation between its results and behaviour in service is not always reliable,

and is sometimes disconcerting. This is at least partly explained by the fact that whereas several investigators have reached the conclusion that the test will give a negative result if the residual tensile stress is less than about 7 tons/in.², it has been proved that season-cracking may occur in service under the influence of stresses well below this value. The possibility of the mercurous nitrate test giving a misleading prediction must, therefore, never be forgotten. The only certain way to ensure freedom from failure by season-cracking is to give the accepted stress-relief anneal as a final operation in any sequence of cold-working operations. In the case of brass this consists of heating to a temperature of about 275° C. for a period of from $\frac{1}{2}$ to 5 hr., depending upon the size, shape, and section of the product.

Until recently it was believed that stress-relief annealing was the only remedy for season-cracking, but it has now been shown⁴³ that the addition of 1% of silicon to α -brass renders it far less susceptible to failure in this way. Unfortunately, the fact that the addition of silicon would be unpopular in the mill and is known to impair somewhat the normal deep-drawing properties of α -brass, may hinder the industrial acceptance of what otherwise would be a welcome remedy.

XIII.—STRETCHER-STRAIN MARKINGS.

“Stretcher-strain marking” is the name given industrially to certain peculiar markings or patterns which sometimes appear on the surface of sheet when it is stretched beyond the yield point. Before the common adoption of this term the markings were called “Lüders lines” after one of the earliest investigators. In fact, as the author has shown elsewhere,⁷ these markings are merely the surface manifestation of solid, slightly tapering blocks or bands extending right through the thickness of the sheet; hence the term “distortion wedge”, proposed in an earlier reference than the one just cited,⁴⁴ would seem to be more appropriate.

Academically, stretcher-strain markings are most interesting and, because a considerable amount of investigation has so far failed to establish the precise reason for their formation, somewhat intriguing. Industrially, they are most unwelcome because they spoil the appearance of an otherwise smooth surface and are so costly to polish out that the expense of salvaging marked pressings is always serious and sometimes prohibitive.

When discussing the incidence of stretcher-strain markings on non-ferrous metals and alloys at the present time, confusion is likely to occur because industrial usage of the term has led to its indiscriminate application to two distinct forms of marking. In the form common in the

press shop the markings closely resemble those seen on steel in that they occur only at the yield point and appear as flamboyant wedge-shaped markings, sometimes disposed in the form of a definite geometrical pattern and sometimes as isolated wedges which continually change direction as the stress system in a sheet or pressing alters (see Fig. 8 (a), Plate LXV). In the other form, usually observed when tensile test-pieces are being strained or sheets are being stretched between the jaws of an hydraulic "leveller", the markings appear as a series of parallel bands extending right across the test-piece or sheet at a nearly constant angle to the direction of applied stress (see Fig. 8 (b), Plate LXV), and often moving up and down the test-piece or sheet like waves. Quite often bands form at this constant angle subtended on both sides of the axis, giving a criss-cross pattern. The most important difference between the two forms is that whereas the flamboyant distortion wedges occur only at the yield point, the parallel bands may sometimes be visible throughout the whole of the plastic range until fracture takes place at one of them.

It seems tolerably certain that both these forms have a common origin and explanation, but until this has been proved it would be prudent to confine the use of the term "stretcher-strain markings" to the first, that is to the flamboyant type of marking as seen in steel, for which the term was originally coined and which is now well established

1. *Flamboyant Wedge-Type Markings.*

In the case of steel, stretcher-strain markings have been recognized for many years, and a considerable amount of scientific study has been devoted, mainly in the United States, to their cause, nature, and prevention. Their incidence and severity have been shown to be closely related to the magnitude of the yield-point elongation evident in the stress/strain curve, and reasonably effective remedies have been found. These take the form of a very light cold rolling, termed "temper rolling" or "skin passing", given to fully annealed sheet by the supplier or, less effective, of "roller levelling" by the user between a series of staggered rolls immediately before the sheet is used. So-called "non-ageing" steels, in which the carbon is either "fixed" by some strong carbide-forming element as in the titanium steels, or entirely removed, as in wet-hydrogen-annealed sheet, do not develop stretcher-strain markings.

With non-ferrous sheet the position is different. Until comparatively recently it was widely believed that the non-ferrous metals and alloys did not develop stretcher-strain markings at all. The few people in industry, for example those engaged in pressing tableware, who knew

that stretcher-strain markings could occur in brass and nickel silver kept their troubles to themselves. Scientists, knowing that stretcher-strain markings in steel were closely connected with the pronounced kink at the yield point in the stress/strain curve of this material, drifted into the belief that the absence of a similar yield-point kink in the stress/strain curves of the non-ferrous metals implied a freedom from susceptibility to such markings. In consequence the criss-cross diagonal bands sometimes seen when sheets were being stretched were generally thought to be an unrelated phenomenon, a view still held by some.

As the use of aluminium alloys, particularly of the aluminium-magnesium type, increased, it became quite clear that stretcher-strain markings of the kind found on steel pressings could, and often did, occur in these alloys. Recognition of this led to a more careful search among non-ferrous press shops and it is now established that the flamboyant wedge type of marking occurs on certain other aluminium alloys and also on brass and nickel silver. The causes of, and remedies for, stretcher-strain markings in aluminium alloys are now being studied by the makers of sheet and by at least one research association; but, owing perhaps to their comparative rarity, those in other non-ferrous metals have failed so far to attract serious scientific interest.

There are a number of differences between steel and non-ferrous metals and alloys in so far as stretcher-strains are concerned. One is that whereas, in steel, markings occur at low extensions and merge into one another completely at about 4% extension to give a surface of uniformly smooth appearance, in non-ferrous alloys markings do not always readily disappear by merging into one another. Another difference is that temper rolling, a sure though transient remedy with steel, does not entirely prevent markings in non-ferrous sheet, although sometimes it changes the form from a few large distortion wedges to a large number of small ones. Yet another is that with non-ferrous metals no remedy comparable with either the immobilization or with the removal of the carbon atoms in steel exists. On the other hand, some investigators are of the opinion that, other things being equal, the tendency for stretcher-strain markings to develop in non-ferrous alloys is greatest when "coring" persists from the cast structure. A last, and very important, difference is that although, in steel, stretcher-strain markings occur only in fully annealed sheet, in non-ferrous metals they may occur both in soft and, to a less extent, in cold-rolled sheet.

Much more work, mostly of an *ad hoc* nature, has been carried out with aluminium alloys than with the other non-ferrous metals and alloys, and it is known that a substantial amount of unpublished, and

sometimes guarded, information exists among sheet suppliers. Claims are made that stretcher-strain markings can be prevented, even in sheet of small crystal size, by careful attention to rolling-mill procedure, particularly in the matter of change of direction of rolling and in stages of reduction; but precise information is difficult to obtain. It is, on the other hand, common knowledge that their incidence and intensity decrease as the crystal size increases, a fact which often leads to the use of sheet having a relatively large crystal size, and hence to a pressed product having a rougher surface than is desired, in order to ensure freedom from stretcher-strain markings. It is also acknowledged that different aluminium alloys vary in their susceptibility to stretcher-strains. For example, the aluminium-magnesium alloys behave badly unless special precautions are taken, whereas the magnesium silicide-type alloys are relatively immune. Observations such as these, together with those on the influence of coring already mentioned, might well be studied in relation to the "dislocation theory" recently proposed by Cottrell⁴⁵ to explain the formation of stretcher-strain markings in steel.

As regards brass and nickel silver still less is known. Men of long experience say that stretcher-strains are less common now than they were some years ago. One of the reasons suggested is that nowadays the crystal size of sheet tends to be smaller and more uniform than of old. If this is the correct explanation it is at variance with the observed facts in the instance of both steel and aluminium alloy sheet, where a large crystal size is known to be beneficial. On the other hand, the chemical purity of sheet of all kinds has increased, and there is reason to believe that some solution and precipitation phenomenon may perhaps play an important part in the as yet imperfectly understood mechanism of stretcher-strain markings.

2. Criss-Cross Band-Type Markings.

These are seen most clearly in certain aluminium alloys, but under suitable conditions they can be observed on other non-ferrous metals and alloys, for example on copper, brass, and nickel silver, when tensile test-pieces are being strained or when sheets are being "stretch-levelled".

It seems tolerably certain that both the incidence and the severity of these bands is in some way connected with the size and number of steps in the stress/strain curve of non-ferrous metals and alloys, just as those in steel are connected with its single, or yield-point, kink. The fact that these steps occur throughout the whole of the plastic range is in keeping with the observed fact that, in non-ferrous metals

and alloys, the formation of the criss-cross band type of markings is not confined, as is the flamboyant wedge type in steel, to extensions in the immediate vicinity of the yield point.

It is interesting to observe the exact similarity in appearance, method of spread, and multiplication, and even in sound of formation, of the criss-cross bands formed on tensile test-pieces of susceptible aluminium alloy strained at ordinary temperatures, and those formed on susceptible steel strained at about 250°C . It will be remembered that at this temperature the normally smooth stress/strain curve of steel of this type shows many steps in the plastic range, and the test-piece extends in audible steps. This similarity suggests that if the aluminium alloy were strained at a low temperature it might suffer plastic extension, as does steel at ordinary temperature, in a smooth uniform manner instead of by the formation, travel, and multiplication of criss-cross bands. Murray ⁴⁶ has carried out tests at -50°C . and states that at this temperature the markings are much less evident, but not entirely absent.

Another observation which adds weight to the belief that the flamboyant wedge and criss-cross band types of marking have a common origin is that in any given sheet the severity of the one type always corresponds with that of the other.

To summarize, stretcher-strain markings of two kinds, probably having a common origin, occur in non-ferrous sheet; but, except in the instance of some of the popular aluminium alloys, their occurrence is not nearly as frequent or as troublesome as it is in steel. Scientific study, which is still lacking, coupled with dissemination of the knowledge already gained by sheet suppliers regarding means for prevention, or even minimization, would be welcome.

XIV.—DEEP DRAWING AND PRESSING OF PATTERNED SHEET.

It has already been explained that the use of blanks or sheet having a mirror-polished surface offers little advantage in most instances. On the other hand, the use of blanks having some decorative pattern rolled or pressed into their surface, or into that of the sheet or strip from which they have been cut, to give either an engraved or an embossed appearance offers much scope in certain fields, such as the making of low-priced fancy goods and tableware.

It is remarkable what severe deformation preformed patterns of this kind will withstand without obliteration, and often without serious injury, even when the pattern is of the embossed as distinct from the engraved type. This is illustrated in Fig. 9 (Plate LXVI), which shows how a pattern of suitable design pre-embossed on a brass blank has

remained strong, and at a casual glance virtually unchanged, not only through the shallow draw by which the wall of a powder compact is made but also through a subsequent rubber-bulging operation used to give the contour seen in the picture.

When severe deep drawing has to be imposed, an "engraved" as distinct from an "embossed" pattern must be used, ironing must be avoided, and proper allowance must be made for the drastic, but constant and geometric, distortion of a preformed pattern which occurs during the deep drawing of a flat blank into a shell.

XV.—BEHAVIOUR OF SOME NON-FERROUS METALS UNDER THE PRESS.

1. *Aluminium.*

Aluminium, usually of commercially pure quality, is deep drawn and pressed extensively. It is peculiar in that for many purposes sheet rolled to the so-called $\frac{1}{4}$ -hard, or occasionally the $\frac{1}{2}$ -hard, condition can be deep drawn more easily, and to a greater extent, than can fully annealed sheet. Drag must be reduced to a minimum, hence a large drawing radius, the lightest possible pressure-plate loading, and very smoothly polished tools are essential.

Aluminium is very amenable to "ironing", and this technique is popular for making food cans such as those illustrated in Fig. 12 (Plate LXVII), which are cupped to full diameter and then ironed through successive dies to the desired depth.

Oil is commonly used as a lubricant, but for the more severe draws various kinds of drawing compounds are sometimes preferred. Aluminium is very prone to critical-strain crystal growth, hence every effort has to be made to accomplish the desired amount of deformation without having recourse to inter-stage annealing. It is fortunate therefore that, when handled properly, aluminium can be deep drawn to a greater extent than any other of the common non-ferrous metals or alloys before annealing becomes unavoidable.

2. *Aluminium Alloys.*

Of the many alloys available, four general types cover the bulk of the sheet which finds its way to the press shop. These are the low-manganese alloys, containing about $1\frac{1}{4}\%$ of the alloying element; alloys containing from $1\frac{1}{2}$ to 5% magnesium, the lower range behaving best and hence being the most popular; the magnesium silicide-type of alloy; and, lastly, complicated alloys of the Duralumin type.

The low-manganese alloy is very little stronger than commercially pure aluminium, and is used mainly because it can be deep drawn and

pressed, with less risk of fracture than can the pure metal, for a wide variety of deep-drawn articles.

The low-magnesium alloy is substantially stronger than pure aluminium, but will not withstand such deep draws. At present one of its main uses is for automobile-body pressings, where its strength is a most valuable asset and its limited deep-drawing properties not of serious consequence in most instances. This alloy is probably the most susceptible of any to "stretcher-strain markings", a troublesome phenomenon discussed in Section XIII. Suppliers are trying various means to minimize the incidence and severity of these markings, but a complete and reliable remedy has yet to be found.

Both the foregoing alloys can be hardened only by cold work. The magnesium silicide-type alloys can be supplied in the solution-treated condition, deep drawn or pressed to the desired shape, and then precipitation-hardened, or aged, to give quite high values for proof stress and ultimate strength. In the soft condition this type of alloy possesses excellent deep-drawing properties and, what is specially welcome, is relatively immune from stretcher-strain markings. For this reason it is sometimes used without subsequent precipitation-hardening, and even in the annealed as distinct from the solution-treated condition, in preference to the magnesium alloy, even though in this soft condition its strength is no greater.

Tools are generally of hardened steel or of cast iron, and the importance of maintaining a really excellent polish on the working surfaces has already been explained. It cannot be said that any particular kinds of lubricant are specially suitable or popular for aluminium or its alloys. The whole available range seems to be used, choice of type being governed mainly by the severity of the drawing operation.

3. *Copper.*

It might be thought that owing to the very great ductility reflected in its high percentage elongation value copper would be a very easy metal to deep draw and press. Actually this is not so, for, like aluminium, its rate of work-hardening is so low that unless special precautions are taken the walls of a cup will fracture without drawing the whole of the blank through the die space. For this reason copper was not popular in the press shop until comparatively recent years; but, now that it has become possible to control its crystal size much more closely than of old, it is looked upon with less disfavour. In fact, by choosing a very small average crystal size, usually between 0.01 and 0.02 mm., and by using $\frac{1}{4}$ -hard instead of fully annealed sheet, copper can be deep drawn in one operation to quite a normal depth, as illustrated by

the one-stage draw shown in Fig. 11 (Plate LXVI). Its low rate of work-hardening makes it amenable to ironing operations, and this technique is often used to extend the very deep cups formed in the making of tubes of substantial length relative to diameter from sheet by the deep-drawing process, a common practice now challenged by that of impact extrusion.

Both hardened steel and cast iron find extensive use for tools. Oils and suds are popular for light and medium draws, but drawing compounds of various kinds are sometimes preferred for heavy draws.

Although a certain amount of deoxidized copper finds its way into some press shops, the bulk of the sheet is still of the kind termed "tough-pitch" and therefore susceptible to what is known industrially as "gassing". This is caused by the action of a reducing atmosphere on the particles of cuprous oxide dispersed throughout sheet of this kind, and may result in a serious loss of ductility. It is still found occasionally in purchased sheet, when a characteristic opening-up of the surface of an Erichsen dome (see Fig. 10, Plate LXVI) quickly reveals its presence. In pressings a similar opening-up of the surface, usually in a series of wave-like fissures, tells a similar story.

Apart from the important matters of a small crystal size and the avoidance of conditions productive of "gassing" during the annealing of either sheet or partly-drawn parts, several minor precautions need to be observed during the deep drawing and pressing of copper sheet if trouble is to be avoided. Thus tools must be well polished and any signs of "loading" immediately removed from dies; pressure-plate loading must be kept to a minimum, particularly when soft instead of $\frac{1}{4}$ -hard sheet is used; but any of the common lubricants can be chosen in accordance with the severity of the draw. Sheet having a really bright polished surface is undesirable; it will not "hold" lubricant, it will not behave in a consistent manner, and it is likely to pucker if deep drawn in tools designed and adjusted for sheet having the usual fine matt surface.

The very low rate of work-hardening of copper, a feature already mentioned, renders deep-drawn articles particularly amenable to relatively substantial deformation by subsequent operations such as bulging, rim-rolling, spinning, and similar operations without annealing. Its freedom from season-cracking is a valuable asset in this, and indeed in many other, connections.

4. *Beryllium Copper.*

This alloy, containing about 2% beryllium, usually with about 0.5% cobalt to increase the uniformity of response to heat-treatment,

is a relative new-comer to the press shop. It behaves somewhat like "basis-quality" brass except that, as it has a substantially higher rate of work-hardening, rather less severe draws have to be given between inter-stage anneals, and better lubricants often have to be employed. Tools can be as for brass. For any but very light press operations sheet should be purchased in the fully annealed condition. The tube illustrated in Fig. 13 (Plate LXVII) shows that if these simple precautions are observed very deep draws can be achieved.

The outstanding feature of beryllium copper is, of course, that it can be cold worked to some desired shape while in a soft, ductile condition and then precipitation-hardened to give quite outstanding mechanical properties, for example, an ultimate tensile strength approaching 90 tons/in.² and a fatigue strength of ± 20 tons/in.² under reversed bending. It does not season-crack. For these reasons it is finding increasing application for pressed diaphragms and for bellows, hitherto made in 80:20 brass, which are commonly corrugated from deep-drawn tubes of the kind illustrated.

5. Brass.

Of all the non-ferrous metals and alloys which are deep drawn and pressed, brass is used in the greatest quantity. It is therefore fortunate that it is one of the easiest to manipulate by this technique. Two grades are commonly used in the press shop: the so-called "basis" quality, containing approximately 62-63% copper, and "cartridge brass" containing approximately 70%. Besides these, small amounts of two other varieties of brass, containing about 65% and 80-90% copper, respectively, are used.

Considered from the aspect of deep drawing and pressing it can be said that basis-quality brass, the cheapest of all, is adequate for many purposes and is indeed preferable for certain pointed or cigar-ended shapes. Cartridge brass, on the other hand, behaves better than basis brass when deep drawn into parallel-sided articles such as cartridge cases, particularly when ironing and inter-stage annealing have to be used. It work-hardens less rapidly, and is rather more liable to fracture in the walls than basis brass. Although it is slightly more expensive its purchase may show an ultimate saving in instances where its greater capacity for plastic deformation enables an inter-stage annealing, necessary with basis brass, or perhaps one of a series of press operations to be dispensed with. The behaviour of brass containing 65% copper is not very different from that of basis brass, except that it tends to be more consistent owing to a reduced tendency for precipitated or incipient β constituent to impair the deep-drawing properties. Brass

containing 80-90% copper, known as "gilding metal", is popular for all kinds of articles in which its golden colour is an asset. It also finds limited application for very deep, parallel-sided tube-like draws, for which it is better than 70 : 30 brass. A possibility which does not appear to have received adequate study is the use of brass sheet of this copper content but having an unusually small crystal size. This combination might well give deep-drawing properties at least equal to those of cartridge brass coupled with a smoother surface after drawing.

The crystal size of both basis and cartridge brass is, rightly, varied to suit particular conditions, more particularly according to the size of the article and, perhaps to a less extent, the thickness of the sheet. Thus thin sheet for shallow draws is often about 0.020-0.030 mm., sheet for deep draws 0.035-0.045 mm., and heavy sheet for large articles 0.045-0.065 mm. "average grain size". If smoothness of surface is unimportant there will generally be a tendency to use a rather larger crystal size than those just given. It cannot be denied that the control of the "average crystal size" of brass sheet has improved very greatly during recent years, but lapses still occur. Irrespective of average crystal size, for reasons explained elsewhere users would welcome a much more uniform crystal size than that commonly given them.

Commenting on manipulation, it can be said that brass will withstand considerable abuse, and is not unduly sensitive to lubricant, speed of drawing, or shape of tools. It is easy to anneal, in that it is not susceptible to critical-strain crystal growth and does not need very close control of time and temperature. "Clean annealing" presents no difficulty, but, owing to the low vapour pressure of zinc, it cannot as yet be bright-annealed successfully under industrial conditions. As with copper, a fine matt surface is preferable to a mirror finish. Tools are usually of hardened steel, although sintered-carbide dies are sometimes employed for the large-quantity production of small articles. Oils, fatty oils, and suds are used extensively for light and medium draws, but drawing compounds are often preferred for heavy draws with thick metal.

The most unwelcome feature of brass is, perhaps, its tendency to season-crack, a failing particularly evident when the copper content is 65% or lower. A final low-temperature stress-relieving anneal is the best remedy, and one that should always be given.

6. *Nickel and Nickel Alloys.*

Nickel, and indeed most of the commonly used nickel alloys, possesses good deep-drawing properties. From the aspect of manipulation in the press shop the alloys can be considered, with the possible exception of

cupro-nickel and nickel silver, as behaving true to type but showing a substantial increase in rate of work-hardening and in the force needed to deep draw a given cup as the number and proportion of alloying elements increases. Pure nickel behaves in a manner not unlike that of deep-drawing-quality steel sheet; indeed, the same tools can often be used for both provided that the clearances are adequate, because nickel does not thin quite as much as steel during its passage over the die radius. Monel metal needs larger drawing radii and clearances, higher pressure-plate loading, more power, better lubricants, and more frequent anneals, modifications which have to be increased still more for alloys of the Inconel type.

Unless draws are unusually light, nickel alloys demand durable tools and the better kinds of drawing lubricant. For short runs with moderately severe operations tools made in hard alloy bronzes are often adequate, but for severe conditions acicular alloy iron, hardened steel preferably chromium plated, and even tungsten carbide are essential. Fatty oils can be used for medium draws, but drawing compounds or special kinds of lubricant are invariably needed for severe conditions.

Nickel alloys differ from most other non-ferrous alloys in that failure during deep drawing does not always occur by transverse rupture of the walls of the shell by tensile stress. Instead a shell may draw in an apparently satisfactory manner only to split downwards from the lip in straight longitudinal cracks at the completion of the draws, or sometimes shortly afterwards. This kind of failure, known as "stress-cracking", occurs only when the metal has been very severely cold worked. The remedy is to anneal before the danger point is approached, although if a flange is left on the periphery of a shell the likelihood of stress-cracking is lessened very considerably. If no further plastic deformation is to be imposed, an immediate stress-relieving anneal at 375°–425° C. will usually prevent cracking and will cause little or no softening; but some authorities consider a temperature of about 500° C. to be necessary for complete immunity.

Stress-cracking is confined to alloys which work-harden rapidly and to a substantial degree, such as some nickel alloys and austenitic steel. It is caused entirely by the action of residual stresses and is not to be confused, as it often is, with season-cracking, which is an entirely different phenomenon requiring the action of an external corrosive agent. The incidence of stress-cracking is encouraged by a rough peripheral edge and by the presence of ironed-out wrinkles, hence special care should be taken to avoid these faults in nickel alloys of the Monel and Inconel type.

Cupro-nickel and nickel silver, having copper and not nickel as their

principal constituent, fall into a different class because they are softer, more ductile, and work-harden at a much less rapid rate than the nickel-predominant alloys which have just been considered. Both have excellent deep-drawing properties; indeed, except for the common difference that the drawing force, pressure-plate loading, and tool wear are all somewhat greater, cupro-nickel can be likened to 70 : 30 or even 80 : 20 brass and nickel silver to 67 : 37 brass. Both cast-iron and steel tools are used, depending on the severity of the draw and on the number of articles to be produced. Similarly, the whole range of lubricants finds application according to the severity of the draw. Neither cupro-nickel nor nickel silver are subject to stress-cracking, but nickel silver is susceptible to season-cracking although not to the extent of the low-copper range of α brasses.

Of the range of cupro-nickels, the 80 : 20 alloy is used much more than the others for deep drawing and pressing. The behaviour of this alloy in press tools is almost unique. It possesses a very low rate of work-hardening; but, unlike other metals which have this feature, for example pure aluminium and pure copper, it also possesses a substantial degree of what elsewhere has been termed "tenacity". Because of this, sheet can be deep drawn in the soft condition without having its performance partially spoilt by the measure of cold rolling needed to prevent the other metals just mentioned from fracturing in the walls of the cup. Cupro-nickel is virtually free from stress-cracking, and some idea of its extraordinary capacity for cold deformation can be gathered from the fact that bullet envelopes are deep drawn to their full depth and the lip of the case rolled over without any inter-stage annealing whatever. In spite of this no splitting occurs during manufacture, storage, or use.

The term "nickel silver" covers a rather wide range of alloys. Those commonly deep drawn and pressed usually contain about 10–15% of nickel with the copper held constant at about 60–65%, the balance being zinc. Nickel silver possesses a high degree of "tenacity" and, given proper tooling, will thin uniformly to a surprising extent before local thinning leading to fracture occurs. This is well illustrated by the three-compartment vegetable dish shown in Fig. 14 (Plate LXVIII), which although "sharpened up" by a second operation has been deep drawn in the first draw to the depth seen in the photograph. It will be appreciated that in the central part of this dish and in areas adjacent to the three radial ridges no metal can be drawn in from other regions in the usual way, hence the quite deep cups have to be formed mainly by stretching and thinning of what metal is already there.

To end this survey of nickel and nickel alloys, mention must be

made of an unfortunate feature common to them all, though of greatest significance in the high-nickel alloys, namely, their susceptibility to attack by sulphur and lead at elevated temperatures. Their behaviour under the press often necessitates the use of a lubricant of high film strength, and it happens not infrequently that this is achieved in part by the addition of free sulphur, sulphur compounds, or occasionally lead compound. It is desirable that lubricants containing sulphur, particularly when in the free form, should be removed as soon as possible after their application, and essential that those containing sulphur or lead in any form should be completely removed before work is heated for annealing. If it is to come into contact with the work being annealed, either as a heating medium or as a protective atmosphere, town's gas should be desulphurized before use.

7. *Zinc.*

The deep-drawing properties of zinc at room temperature are poor. However, if blanks of 99·99% purity zinc having a small crystal size are heated to within the range 40°–90° C., the exact temperature depending on the shape of the article and the crystal size of the sheet, quite reasonable draws can be accomplished, because within this range the metal possesses a combination of ductility and tenacity which is out of balance at higher and lower temperatures. Zinc is self-annealing at the temperature attained during most deep-drawing operations; indeed, sometimes it is difficult to avoid an undesirable coarsening of the crystal structure.

Hardened-steel tools are generally used. Vaseline or dilute "suds" are useful lubricants, the latter having the advantage that blanks can be heated to drawing temperature in a bath of it placed beside the press. For some reason "oily" and other good lubricants often give poor results with zinc.

At first sight it seems curious that zinc, which when present in an alloy is the cause of season-cracking, is itself immune from this unwelcome happening. The explanation may lie in the fact that as the pure metal work-hardens very slowly indeed and is virtually self-annealing, no residual stresses of any magnitude exist in deep-drawn articles.

8. *Silver.*

Fine silver, like other very ductile metals, has poor deep-drawing and pressing properties, and for this reason is nearly always shaped by other methods. When it is desired to use the deep-drawing and pressing process, sterling silver, usually with from 0·5 to 3·5% of the permissible 7·5% of copper replaced by cadmium to give extra hardening

and "tenacity", is chosen instead of fine silver. This alloy behaves reasonably well under the press, but its capabilities are seldom utilized to the full owing to certain peculiarities associated with the silverware industry. For example, the very small numbers of any article usually produced at one setting up of the appropriate tools, the use of tools designed for other thicknesses of sheet, the need to avoid the production of any scrap at all even among the "first few off" entirely new tools, combine to dictate the use of very easy stages of deformation interspersed with frequent inter-stage anneals. Again, these anneals are commonly carried out in gas-heated semi-muffle furnaces, or even under a blow-pipe, without any accurate control of time or temperature, so that a desirable crystal structure, so necessary if good deep-drawing and pressing properties are to be preserved, is seldom maintained. For this reason it is particularly fortunate that, unlike fine silver, sterling silver in the condition in which it is commonly used has a duplex microstructure which hinders grain coarsening, particularly if the annealing temperature is kept below 690° C.

When sterling silver is annealed in air it is likely to develop a defect known in the trade as "fire-stain", which may or may not become apparent until the finished product is buffed. This defect is caused by oxygen penetrating inwards into the sheet and oxidizing the copper in the copper-rich constituent of the alloy to give specks of black copper oxide. Because many small firms consider that the cost of furnaces equipped with an adequate protective atmosphere is too high to justify their purchase, considerable interest attaches to the recent discovery that the replacement of 1% of the copper in sterling silver by a similar proportion of aluminium reduces the rate of oxygen penetration to such an extent that the "fire-stained" surface layer is thin enough to be quickly polished off without serious loss of metal. This aluminium addition, which also reduces the rate of crystal growth at high temperatures, does not impair the deep-drawing properties of sterling silver to any serious extent.

Old-established custom continues in the use of steel tools with oil as a lubricant in spite of the saving in time and cost which cast zinc tools appear to offer. Scoring must be avoided because when scores are polished out some loss of precious metal is unavoidable. Stages in the production of a deep-drawn shell $\frac{7}{8}$ in. in dia. and 2 in. deep from a blank of sterling silver $3\frac{1}{4}$ in. in dia. and 0.014 in. thick are shown in Fig. 15 (Plate LXVIII). Annealing is given between each draw. In the final operation the recess in the bottom of the shell is formed by rubber.

Considerable use is made of the bulging process, well illustrated by

the salt-cellar shown in Fig. 2 (Plate LXIII). Rubber is generally used for this purpose, although for certain applications wax is preferred. In-tapering and outward-tapering processes, carried out with the help of solid tools, are also popular. The use of deep-drawn cups instead of flat blanks as a starting point of spinning often shows substantial savings, besides enabling shapes to be spun which could not be reached by this process alone starting from a flat blank.

Deep drawing and pressing is usually considered to be economic only when the cost of the necessary tools and the occupation of presses can be spread out over a very large number of articles. The application of this craft in the silverware industry is therefore unique in that some firms will periodically set up as many as twenty separate sets of press tools to produce perhaps no more than one dozen articles at each run. As unit die-sets are hardly ever used in this industry it might well be imagined that, as the time spent in mounting, setting, and dismounting loose tools invariably takes more hours than their actual use occupies minutes, deep drawing would be an unsuitable and uneconomical method of production. In fact, slow as it is, it often proves to be many times as quick as hand-beating. This may still be so even when hand-beating is applied as a last operation to a deep-drawn product to give the illusion that it has been formed entirely by hand.

XVI.—CONCLUSION.

In this paper a number of matters of importance, or of special interest metallurgically, connected with the deep drawing and pressing of non-ferrous metals, have been reviewed and discussed. Although prominence has purposely been given to what is popularly termed the "practical" aspect, some consideration of scientific and theoretical matters has been included. The shortcomings and inadequacy of existing relevant knowledge have been pointed out, and the need both for new knowledge and for better application of what is already known has been emphasized. In particular, it has been explained that so-called deep-drawing properties cannot yet be defined or measured in a precise manner, and that these seem to depend upon the attainment of a nice balance, suited to the requirements of any particular press operation, between what have been described somewhat vaguely as "ductility" (meaning ability to flow) and "tenacity" (meaning ability to transmit stress without sustaining localized "necking").

Users of sheet, particularly small firms, have perforce to leave the planned study of such matters to the Universities and Research Associations; but, to end this paper on a "practical" note, a plea is made for still closer co-operation between the user and the supplier of sheet

destined for the press shop. Most users, particularly the many smaller ones, could be more insistent in their demands for sheet having better properties and in their complaints about metal of less-than-average quality. Suppliers of sheet should visit their customers' shops more often, for unless they actually see what is happening, and watch the behaviour of their metal, they must often fail to appreciate why the user really does need this or that particular combination of properties and why he is often so anxious to obtain sheet of better, and of more uniform, quality. Knowledge gained in this way is much more likely to hasten improvements, which in fact are desired by all, than are vague complaints passed on through travellers or even by letters to the management.

On the other hand, a user should periodically visit the foundries and mills of his suppliers because in no other way can he on his part understand the difficulties, many of which are directly related to the faults or conditions he wants remedied in the sheet he purchases, with which suppliers have to contend. Mutual goodwill, coupled with as thorough an understanding as possible of each others' needs and difficulties is, surely, the surest and quickest way to progress.

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STRESS-CORROSION OF MAGNESIUM ALLOYS.*

1291

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

The stress-corrosion properties of magnesium-5% aluminium alloy in distilled water and other solutions have been investigated. Stress-corrosion tests were also carried out on other commercial magnesium-base alloys and on high-purity magnesium.

Rapid transcrystalline cracking of stressed magnesium-5% aluminium alloy in distilled water took place, whether the alloy contained a precipitated second phase or not. This cracking bore no apparent relationship to the metallographic structure, following neither grain boundaries nor twin planes. Stress-corrosion was associated with a localized penetrative type of transcrystalline attack, which was never observed to be more than 2-3 grains deep. The stress-corrosion resistance decreased with increase in iron content and in amount of plastic deformation, but was improved by annealing at 200°C. after plastic deformation. The presence of dissolved oxygen was found essential for stress-corrosion to operate, e.g. stressed loop specimens which failed in aerated distilled water in 10 days, did not crack in de-aerated water in 60 days. Transcrystalline stress-corrosion fractures occurred in saturated magnesium carbonate, 0.5% potassium fluoride and 0.5% potassium hydrogen fluoride solutions, and in 0.5% hydrofluoric acid, and intercrystalline fractures in 0.05% potassium chromate solution.

The susceptibility to stress-corrosion failure of the various commercial alloys tested was consistent with their reported service behaviour, the magnesium-manganese and magnesium-zinc-zirconium alloys being more resistant than the magnesium-aluminium alloys. All the alloys tested and also high-purity magnesium suffered stress-corrosion cracking in 0.5% potassium hydrogen fluoride solution.

No detailed mechanism of stress-corrosion cracking in magnesium-base alloys is put forward, though the results show that the process is in part electrochemical. It is thought that cracking may be associated with minor impurities, e.g. iron, which are known to have a deleterious effect on the ordinary corrosion-resistance.

I.—INTRODUCTION.

ALTHOUGH there is little published information on the stress-corrosion properties of magnesium and its alloys, it has been generally agreed that pure magnesium and the alloys containing 1.5-2.0% manganese are not susceptible to stress-corrosion;¹⁻⁶ whereas magnesium-aluminium-zinc and magnesium-aluminium alloys are prone to it, susceptibility increasing with the aluminium content.^{2,4,6,7} Many different corrosive environments for testing susceptibility have been

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used. Thus, cracking has been reported in distilled water,^{3,8,9} in an indoor atmosphere,¹ and under atmospheric conditions.⁸ Short-time laboratory tests have been carried out by Mears *et al.*¹⁰ using a solution of sodium chloride and potassium chromate (i.e. 35 g. NaCl and 20 g. K_2CrO_4 /l., pH 8.1), which gave rapid stress-corrosion failures with little general corrosion. This testing medium seems, however, to bear little relation to possible service conditions.

In contrast to the aluminium-base alloys the path of the crack in magnesium-base alloys is generally transcrystalline. Beck² states that the direction is determined by crystallographic factors, probably being parallel to twinning planes. This is refuted by Graf,⁹ who states that "the course of the cracks did not follow twin lamellæ even when favourably situated". Although transgranular cracking is most common, Mears *et al.*¹⁰ found that if a magnesium-6% aluminium-1% zinc alloy was tested in the solution given above, the cracking was transcrystalline, while if the pH of the solution was adjusted to 5.0 the cracking was intercrystalline.

Plastic deformation is said to be an important factor in influencing the stress-corrosion of magnesium-base alloys.¹¹ This has led several authorities to advocate a low-temperature stress-relieving anneal. The advantage of such annealing has been pointed out by Mears,¹⁰ Beck,² Siebel,⁴ and others. Temperatures from 100° to 200° C. for a few hours are advocated, but it is not clear whether the beneficial effect is due to relief of stress or to precipitation of the β phase $Mg_{17}Al_{12}$.

Although no mechanism for the transgranular stress-corrosion cracking of magnesium alloys has been suggested, Mears¹⁰ showed that the cracking of magnesium-6% aluminium-1% zinc alloy could be prevented by cathodic protection, thus indicating that the mechanism of cracking is at least partly electrochemical.

Little work has been carried out on the protection of magnesium alloys against stress-corrosion. Beck² has shown that cladding with a magnesium-2% manganese alloy gives effective protection, and Wieschhaus¹² and Knight¹¹ that shot-peening increases the stress-corrosion-resistance. Krivobok¹³ states that the usual dichromate treatment of magnesium alloy sheet increases the stress-corrosion life, while Loose and Barbian⁶ report that painting greatly extends the time to cracking both in direct-tensile tests and in welded assemblies exposed to the atmosphere.

The major part of the work described in the present paper has been carried out on the magnesium-5% aluminium alloy corroded in distilled water. A few tests have also been made on a range of commercial alloys.

II.—EXPERIMENTAL PROCEDURE.

1. *Materials Used.*

The materials used, the analyses of which are given in Table I, were in the form of 18 S.W.G. sheet, except for the alloys marked *A*, *B*, *C*, and *D*, which were 16 S.W.G. All alloys were in the annealed condition when received from the makers.

TABLE I.—*Chemical Analysis of Materials Used.*

Alloy Mark	Al, %	Mn, %	Zn, %	Zr, %	Ce, % (Total Rare Earth)	Fe, %	Ni, %	Cu, %	Si, %	P, %
Al . . .	6.30	0.30	0.81	—	—	n.d.	n.d.	n.d.	n.d.	n.d.
MWY1 . .	5.10	0.30	—	—	—	0.013	0.001	n.d.	n.d.	n.d.
MWY3 . .	4.83	0.42	—	—	—	0.0019	0.001	0.003	0.020	0.002
A . . .	—	1.68	—	—	—	0.016	0.0014	0.006	0.007	0.013
B . . .	—	1.60	—	—	0.44	0.020	<0.001	0.006	0.009	0.001
C . . .	3.0	0.17	0.90	—	—	0.018	0.0013	0.005	0.020	0.017
D . . .	3.8	0.28	—	—	—	0.015	0.0013	0.004	0.013	0.005
F . . .	—	0.011	2.9	0.75	—	0.004	0.0009	0.004	0.002	0.001
High-purity magnesium	<0.05	<0.01	<0.05	—	—	0.004	0.0002	<0.01	<0.01	n.d.

n.d. = not determined.

2. *Specimen Preparation Before Corrosion Testing.*

Unless otherwise stated, chromate films were first removed by immersing in 15% chromic acid solution at room temperature; the specimens were then cleaned by rubbing with a suspension of coarse alumina in distilled water on Selvyt cloth, and finally degreased in acetone. The alumina on Selvyt gave a finish similar to that obtained by abrasion with 0000 emery, but in certain cases did not remove deep rolling marks.

3. *Methods of Stress-Corrosion Testing.*

Stressed-loop tests were carried out by the method described by Perryman and Hadden.¹⁴ Unless otherwise stated, strips were cut perpendicular to the final rolling direction. Direct-tensile stress-corrosion tests were also carried out using standard 2-in. sheet tensile test-pieces (B.S.485 (1934) Type A), also cut at right angles to the final rolling direction. The specimens were stressed using a calibrated spring as described elsewhere.¹⁴ The direct-tensile specimens were partially immersed during test by securing them through rubber bungs in glass tubes containing the corrosive agent, the level of which came about two-thirds of the way up the gauge-length. In general, three stressed and two unstressed specimens of each material were exposed.

One of the unstressed specimens was removed when the first stressed specimen broke, and the other when the last broke, and their residual mechanical properties determined. The loss of strength due to stress-corrosion was then found by subtracting the initial applied stress from the residual strength of the unstressed corroded specimens.

III.—RESULTS.

1. *Effect of Corroding Medium.*

In view of the extremely rapid failures (i.e. in a period of hours) obtained by other workers when using sodium chloride solution containing potassium chromate, it was considered that another solution should be used which would (a) simulate service conditions more closely, (b) give less rapid failures, and (c) produce little pitting corrosion. Corrosion tests were therefore carried out on magnesium-6% aluminium-1% zinc alloy in distilled water and in sodium chloride solutions of strengths ranging from 0.0025 to 2%. Using solutions containing 0.1% or more sodium chloride, corrosion began almost immediately on immersion and continuous gas evolution occurred. With concentrations of 0.05% or less, there was much less corrosion than with the stronger solutions, and it was found mostly in isolated areas. Specimens which had been immersed in distilled water showed: (1) small bright pits, (2) black unattacked areas surrounding these pits, and (3) greyish white areas covering the remaining surface which under the binocular microscope were seen to contain a large number of cracks.

The most satisfactory media therefore appeared to be either distilled water or very weak sodium chloride solutions. Direct-tensile stress-corrosion tests using distilled water spray or partial immersion in distilled water showed that rapid transcrystalline cracking occurred, while there was only slight corrosion in the absence of stress. For example, specimens of the magnesium-6% aluminium-1% zinc alloy in the "as-received" condition partially immersed in distilled water had a stress-corrosion life of about 20 days at an initial tensile stress of 8 tons/in.², which is approximately equal to the 0.1% proof stress of the material. Distilled water was therefore selected as an appropriate corroding agent for future work.

2. *Tests on Magnesium-5% Aluminium Alloy.*

(a) *Effect of Solution-Treatment Temperature.*

Although microscopical examination showed that a solution-treatment of 360° C. for 3 hr. was sufficient to take all the precipitated

Mg₁₇Al₁₂ into solution, it had been suggested¹⁵ that higher temperatures were necessary for complete solution, and it was considered desirable to examine the effect of solution-treatment temperature on stress-corrosion life. Direct-tensile stress-corrosion tests in distilled water were therefore carried out at an initial tensile stress of 7.5 tons/in.² on material solution-treated for 3 hr. at 360°, 400°, and 440° C. and quenched in cold water. The results are given in Table II.

TABLE II.—*Effect of Solution-Treatment Temperature on Mechanical and Stress-Corrosion Properties of Magnesium-5% Aluminium Alloy. (MWY3).*

Solution-Treatment Temp., ° C.	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation on 2 in., %	Initial Applied Stress, tons/in. ²	Stress-Corrosion Life, days *	Loss of Strength Due to Stress-Corrosion, tons/in. ²
360	16.6	6.0	16	7.5	7, 24, 16 (16)	8.8
400	16.1	5.5	18	7.5	22, 34, 30 (29)	8.3
440	16.1	5.5	19	7.5	20, 17, 22 (20)	8.4

Mechanical properties given are the mean of two determinations.

* Figures in brackets give mean life.

All the specimens failed with a transcrystalline fracture, and there was no significant difference in their stress-corrosion behaviour. It was therefore decided to adopt 360° C. as the standard solution-treatment temperature, so that quenching stresses and loss of magnesium would be minimized.

(b) Behaviour in Various Metallurgical Conditions.

Loops made from MWY1 sheet were tested in distilled water; some strips were heat-treated before bending, and others after bending. Strips were solution-treated at 360° C. for 3 hr., followed by water quenching, and some were subsequently aged at 150° C. for 2 hr. The latter treatment produced a continuous film of the second phase (Mg₁₇Al₁₂) at the grain boundaries.

The loops were stressed by closing the ends and inserting them in a wooden frame, which was inverted and supported on the edges of a glass tank so that the loops dipped approximately 1½ in. into the distilled water. Four or five stressed loops and an unstressed control specimen (i.e. a formed loop whose ends had not been closed) were included for each condition tested.

During the first few days, a grey film formed over most of the surface, but this became darker and eventually black. The as-received specimens blackened more rapidly than those which had been solution-treated at some stage in their preparation. The black film, analysed

by the X-ray powder method, was found to be largely magnesium hydroxide. Small pits capped with nodules of white corrosion product occurred at random on the specimens. The nodules usually contained a small "pin-hole" from which gas bubbles emerged. Surrounding the pits were bright areas which gradually merged into the black areas covering the major part of the surface.

The results of these tests are given in Table III. When comparing the results it must be remembered that the mechanical properties of the material in the various conditions tested varied widely, thus giving rise to different stresses in the loops. The specimens likely to have similar mechanical properties are as follows: (a) 1 and 2; (b) 3, 4, and 5; (c) 6 and 7.

TABLE III.—*Effect of Metallurgical Condition on Stress-Corrosion Life of Stressed Magnesium-5% Aluminium Loops (MWY1 Sheet).*

Specimen Preparation	Individual Loop Life, days	Average Loop Life, days
(1) Loops solution-treated	9, 9, 10, 11, 11	10
(2) Loops solution-treated and aged *.	9, 11, 12, 15, 18	13
(3) Loops made from solution-treated strips.	16, 20, 23, 24, 25	22
(4) Loops made from solution-treated strips and then aged *.	11, 11, 12, 14, 14	12
(5) Loops made from solution-treated and aged * strips	9, 12, 20, 20, 20	16
(6) Loops made from "as received" material	6, 6, 6, 7	6
(7) Loops made from "as received" material and then aged *.	6, 6, 6, 7	6
(8) As-received strips, aged,* and made into loops	6, 7, 7, 8	7

* Ageing treatment was 2 hr. at 150° C., and produced a continuous film of the second phase $Mg_{17}Al_{12}$ at the grain boundaries.

Rapid stress-corrosion failures occurred whether the second phase ($Mg_{17}Al_{12}$) was precipitated at the grain boundaries or not, the cracks being transcrystalline. This is in direct contrast to the behaviour of aluminium-magnesium alloys, where precipitate at the grain boundaries is necessary for stress-corrosion to take place, and the cracks are intercrystalline. Additional experiments showed that the original chromate film did not protect the alloy from stress-corrosion.

Examination of Loop Specimens.—Two stressed specimens and the unstressed specimen from each group were examined microscopically. Fig. 1 (Plate LXIX) shows a typical transgranular stress-corrosion crack in the as-received material which had been plastically deformed and aged. On unstressed specimens and on both tension and compression sides of stressed specimens a narrow surface zone containing numerous

short transgranular cracks was observed (Fig. 2, Plate LXIX). The phenomenon was common to all specimens irrespective of the metallurgical condition, although more marked in specimens which had been solution-treated. Specimens aged after solution-treatment suffered about the same amount of this localized penetrative attack as solution-treated specimens, even though they had been exposed for a longer time, indicating that the ageing slightly decreases the tendency to undergo this attack. Fig. 2 illustrates the localized transgranular attack in an unstressed specimen which had been solution-treated and aged. Fig. 3 (Plate LXIX) shows a network of localized corrosion cracks on the corroded surface. In Fig. 4 (Plate LXIX) is seen similar transgranular attack and a typical stress-corrosion crack in a stressed loop (solution-treated condition). This photograph indicates that the stress has caused a rapid extension of one of the small cracks initiated by ordinary corrosion (see also Fig. 6, Plate LXX).

The penetrative attack described above was found generally in the grey-black areas on all specimens, and was absent from areas which remained bright and apparently unfiled.

(c) *Effect of $Mg_{17}Al_{12}$ Precipitated within the Grains.*

Although grain-boundary precipitate did not appear to affect the stress-corrosion susceptibility to any marked extent, it was thought

TABLE IV.—*Effect of Ageing on Stress-Corrosion Properties of Magnesium-5% Aluminium Alloy (MWY3 Sheet).*

Metallurgical Condition	Original Mechanical Properties			Initial Applied Stress, tons/in. ²	Stress-Corrosion Life, days *	Approx. Loss of Strength Due to Stress-Corrosion, tons/in. ²
	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation on 2 in., %			
Solution-treated + 10% overstrain	17.6	16.0	9	7.5 4.0	21, 11, 14 (15) 22, 47, 61 (43)	9.5 13.2
Solution-treated + 10% overstrain + 4 days at 200° C.	16.8	9.0	13	7.5 4.0	18, 15, 25 (19) 55, 76, >125 † (>89)	8.9 — —
Solution-treated + 10% overstrain + 14 days at 200° C.	17.1	10.5	10	7.5 4.0	11, 25, 25 (20) 76, 98, >125 † (>100)	9.2 — —

Mechanical properties are the means of two determinations.

* Figures in brackets give mean life.

† Specimens pulled for residual mechanical properties but broke at grip.

that precipitation within the grain might have a larger effect, since the cracking was transcrystalline. Accordingly, specimens were solution-treated, over-strained 10%, and aged at 200° C. for 4 and 14

days. These treatments resulted in precipitation at grain boundaries and also along slip planes, with much more precipitate present after ageing for 14 days than for 4 days. The results of direct-tensile stress-corrosion tests in distilled water are included in Table IV.

Ageing at 200° C. led to an increased stress-corrosion life, even though the specimens were stressed nearer to the 0.1% proof stress than the solution-treated specimens. Examination of the failed specimens showed that the cracking was transcrystalline and that the localized penetrative attack was rather less on the specimens which had been aged.

(d) *Effect of Iron Content.*

The detrimental effect of iron on the corrosion-resistance of magnesium and its alloys has been demonstrated by Hanawalt and his co-workers,¹⁶ and more recently Heidenreich and his colleagues⁷ have suggested that the stress-corrosion susceptibility of magnesium-

TABLE V.—*Effect of Iron Content on Stress-Corrosion Properties of Magnesium-5% Aluminium Alloy.*

Sheet No.	Fe, %	Metallurgical Condition	Original Mechanical Properties			Initial Applied Stress, tons/in. ²	Stress-Corrosion Life, days *
			U.T.S. tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation on 2 in., %		
MWY1	0.013	As received	18.0	10.0	14	7.5 5.5 4.0	12, 14, 15 (13) 24, 17, 31 (24) 39, 39, 39 (39)
MWY3	0.0019	As received	17.1	7.1	13	7.5 5.5	8, 21 (14) 38, 34, 27 (33)
MWY1	0.013	Solution-treated	16.8	9.6	14	7.5 4.0	3½, 5½, 5½ (5) 26, 33, 33 (31)
MWY3	0.0019	Solution-treated	16.8	6.0	16	7.5	7, 24, 16 (16)
MWY1	0.013	Solution-treated and overstrained 10%	18.2	16.5	5	7.5 4.0	4, 5½, 5½ (5) 10, 13, 26 (16)
MWY3	0.0019	Solution-treated and overstrained 10%	17.6	16.0	9	7.5 4.0	21, 11, 14 (15) 22, 47, 61 (43)

* Figures in brackets give the mean stress-corrosion life.

aluminium alloys is connected with the iron content. The stress-corrosion properties of the two sheets, MWY1 with 0.013% iron and MWY3 with 0.0019% iron (both having the same nickel content) were compared, using direct-tensile stress-corrosion tests in distilled water. The results, given in Table V, show that in all the conditions

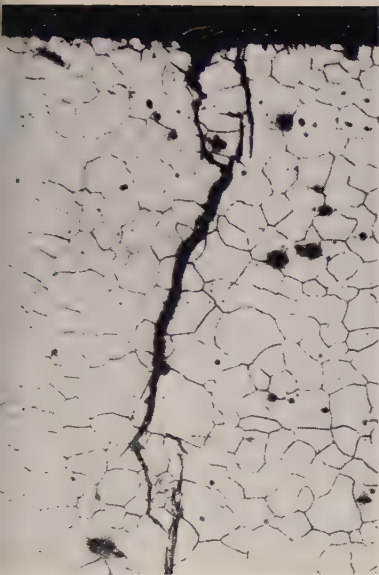


FIG. 1.—Stress-Corrosion Crack in Magnesium-5% Aluminium Alloy Loop Corroded in Distilled Water. As-received and aged at 150° C. for 2 hr. after bending into loop. $\times 170$.



FIG. 2.—Unstressed Magnesium-5% Aluminium Alloy Loop Corroded in Distilled Water. Solution-treated and aged at 150° C. for 2 hr. $\times 300$.

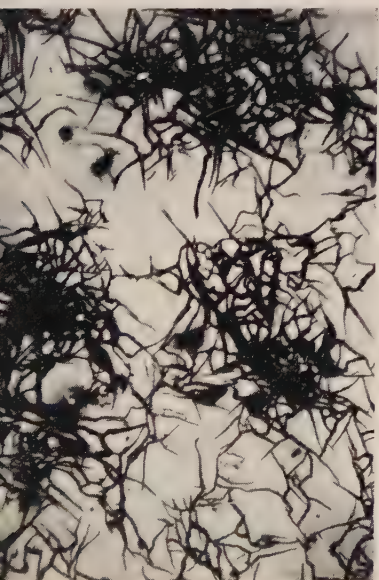


FIG. 3.—Section Parallel to Corroded Surface of an Unstressed Magnesium-5% Aluminium Alloy Loop Corroded in Distilled Water. Solution-treated and aged at 150° C. for 2 hr. $\times 150$.



FIG. 4.—Stressed Magnesium-5% Aluminium Alloy Loop (Solution-treated) Corroded in Distilled Water. Showing stress-corrosion crack and localized penetrative attack. $\times 150$.



FIG. 5.—Surface Attack on Unstressed Solution-treated Magnesium-5% Aluminium Alloy Immersed in Distilled Water for 21 days. $\times 100$.



FIG. 6.—Same as Fig. 5 except that specimen was stressed at 7.5 tons/in.². $\times 100$.



FIG. 7.—End of Stress-Corrosion Crack in As-Received Magnesium-5% Aluminium Alloy. $\times 500$.

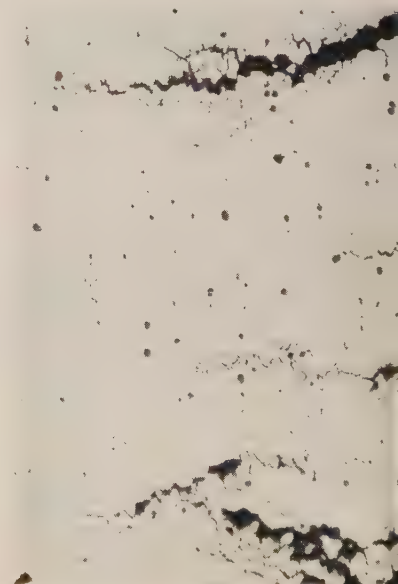


FIG. 8.—Stressed Magnesium-5% Aluminium Alloy (As-Received) Loop Corroded in 0.05% Potassium Chromate. Shows Intercrystalline Cracking. $\times 50$.

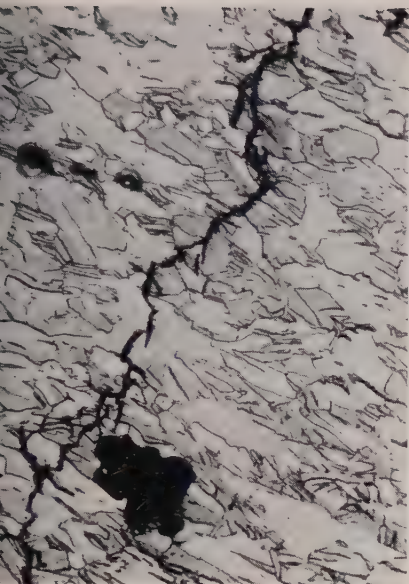


FIG. 9.—Stress-Corrosion Crack in As-Received Magnesium-2% Manganese Alloy Stressed in 0.5% Potassium Hydrogen Fluoride. $\times 400$.

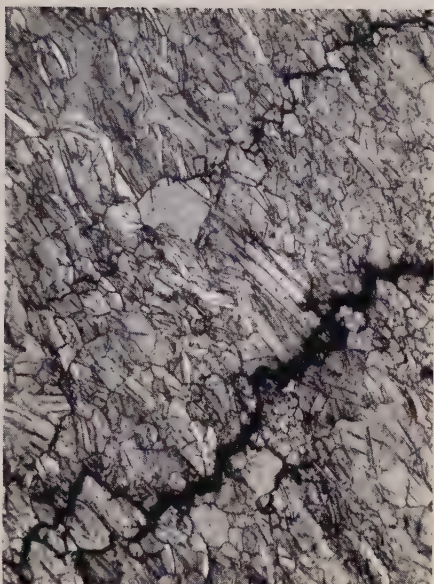


FIG. 10.—Intercrystalline Cracking in As-Received Magnesium-3% Zinc-0.7% Zirconium Alloy Stressed in 0.5% Potassium Hydrogen Fluoride. $\times 500$.



FIG. 11.—Same as Fig. 10. Note number of deep cracks. $\times 20$.

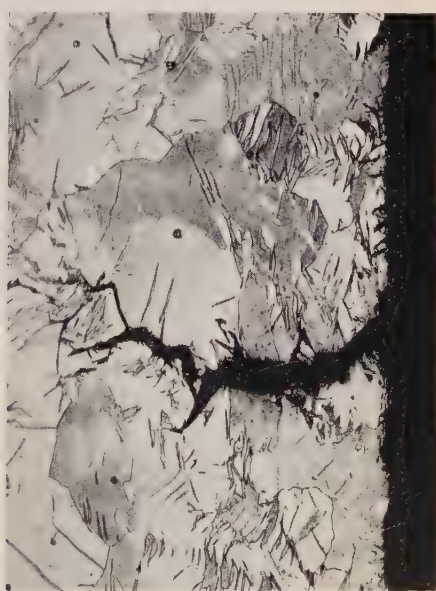


FIG. 12.—Subsidiary Stress-Corrosion Crack in As-Received High-Purity Magnesium Stressed in 0.5% Potassium Hydrogen Fluoride. $\times 350$.

tested the high-iron specimens (MWY1) were more susceptible to stress-corrosion than the corresponding low-iron specimens (MWY3). In considering these differences it must be remembered, however, that the low-iron sheet was tested at larger percentages of the proof stress than the high-iron sheet MWY1. Table V also shows that plastically deformed material is more susceptible to stress-corrosion than annealed material.

Examination of Tensile Specimens.—In the partial-immersion direct-tensile tests described, failures usually occurred at or just below the water level. Moreover, unstressed corroded specimens pulled for residual mechanical properties usually fractured at or just below what had been the water level, indicating that corrosion had been most intense in that area. These facts suggested that the oxygen supply might be an important factor. The appearance of the specimens was similar to that of the loops described above, and the localized penetrative type of attack found on both stressed and unstressed specimens developed first near the water level. As the time of immersion increased, the network of corrosion crevices became more dense and appeared as grey-black areas on the specimen; the stress-corrosion fracture was also covered with this grey-black film. On examining the specimens microscopically it was found that in all conditions there was more of the localized penetrative attack in the high-iron specimens (MWY1) than in the low-iron (MWY3), both with stressed and unstressed specimens; the cracking was always transcrystalline. Although the localized penetrative attack was present in both stressed and unstressed specimens, the cracking was deeper when the specimen was stressed (see Figs. 5 and 6, Plate LXX). The grey-black film was formed more uniformly on overstrained specimens than on those not overstrained, and microscopical examination showed that the localized penetrative attack was more pronounced on overstrained specimens.

Fig. 7 (Plate LXX) shows the termination of a subsidiary stress-corrosion crack, which apparently bears no relation to the structure revealed by George's¹⁷ reagent, the crack following neither grain boundaries nor twin planes.

(e) *Further Observations on Localized Penetrative Attack.*

As described earlier, stressed-loop specimens of magnesium-6% aluminium-1% zinc alloy immersed in sodium chloride solutions of strength 0.1-3% showed no cracking but only intensive pitting. Magnesium-5% aluminium specimens behaved in the same way. To investigate this further, polished microspecimens of solution-treated magnesium-5% aluminium (MWY1 sheet) were immersed in 50 c.c. of

distilled water or 0.05, 0.1, 0.25, or 0.5% sodium chloride solution, and examined microscopically at intervals. Localized penetrative attack began on the specimen in distilled water after two days and proceeded until after 20 days it covered some 40% of the area, being associated with a thick black film; the remaining area was bright and unattacked. A little penetrative attack developed on the specimen in 0.05%, and one small spot on that in 0.1% sodium chloride solution. No penetrative attack occurred on the specimens in stronger solutions, but these suffered severe pitting.

After corrosion the specimens were lightly ground on 000 emery paper, polished and re-examined. The specimens corroded in distilled water exhibited networks of cracks similar to those in Fig. 3, while specimens corroded in sodium chloride solutions showed pitting attack. On sectioning at right angles to the corroded surface, penetrative attack similar to that in Fig. 2 was seen in the specimen corroded in distilled water, while specimens corroded in the stronger chloride solutions showed large rounded pits. Thus, while chloride in solution intensifies pitting attack, it reduces the tendency to undergo localized penetrative attack and, if present in sufficient concentration, prevents its occurrence altogether.

(f) *Effect of Dissolved Oxygen.*

It has been mentioned that during partial-immersion direct-tensile stress-corrosion tests, failures generally occurred at the water line and also at this point the localized penetrative attack developed first and was most severe, indicating that dissolved oxygen was playing an important part in this type of corrosion. Moreover, it is known¹⁸ that the presence of oxygen is essential for the stress-corrosion cracking of aluminium-7% magnesium alloy.

To investigate this further a series of loops were tested in aerated and de-aerated distilled water. The procedure for de-aerating was to reduce the pressure over the water until no more bubbles were evolved and then to bubble through oxygen-free nitrogen for 10 min. The specimen was then immersed and the pressure again reduced; finally, nitrogen was bubbled through for another 10 min. and the flask was then sealed.

Three stressed loops in the "as-received" condition (MWY1 sheet) and three solution-treated loops (MWY1 sheet) were immersed in separate open flasks each containing approximately 300 c.c. of aerated distilled water. The "as-received" loops cracked in an average of 6 days, and the solution-treated loops in an average of 15 days.

No failure of the as-received loops in de-aerated distilled water

occurred in 25 days. The specimens remained practically unattacked, no grey-black films forming as in aerated water. The surface was also practically free from small white nodules of corrosion product and fewer gas bubbles (presumably hydrogen) were observed adhering to the metal surface. Micro-examination of the specimens after removal from the solution showed no localized penetrative attack.

The solution-treated specimens in de-aerated solution behaved similarly, and no failures had taken place in 47 days. It was thought that carbon dioxide might play some part in the stress-corrosion of this alloy, and so carbon dioxide free from oxygen was passed through the de-aerated distilled water. After approximately 2 hr. the surface of the specimens became covered with a dark grey film and fairly vigorous effervescence occurred. The effervescence later diminished and the surface of the specimens became covered with a white corrosion product, which by X-ray analysis was found to be $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. The loops had not cracked after a further 17 days. The supply of carbon dioxide was then stopped and air was bubbled through for a further 16 days, at the end of which the loops had still not cracked. The specimens were placed in fresh distilled water and air bubbled through; two of the specimens then failed in a further 5 days and the other in a further 16.

These experiments show that stress-corrosion of magnesium-5% aluminium alloy is considerably retarded, if not prevented, when oxygen is excluded, and that oxygen is necessary for the development of the localized penetrative attack. On the other hand, carbon dioxide by itself is probably not able to cause cracking. Although the corrosion of magnesium alloys is usually of the hydrogen-evolution type even in neutral solutions, the present results suggest either that some corrosion of the oxygen-absorption type is occurring or that the absence of oxygen markedly decreases the amount of corrosion due to hydrogen evolution. Mears¹⁹ has shown that oxygen has this effect during the corrosion of aluminium in distilled water.

(g) *Effect of Earlier Corrosion in Aerated Distilled Water on Stress-Corrosion Behaviour in De-aerated Distilled Water.*

As-received stressed loops (MWY3 sheet) were exposed in aerated distilled water for 4 and 10 days, after which time they were transferred to de-aerated distilled water. Two other loops were exposed in de-aerated water throughout. Control as-received stressed loops (MWY3 sheet) in aerated distilled water failed in an average of 11 days.

The two loops which had not been first immersed in aerated water had not failed after 60 days, after which time they appeared bright

and relatively unfiled. Air was then bubbled through the solution and both loops failed after a further 10 days, when the loop surfaces were light grey in colour and covered with localized penetrative attack.

Two loops which had been initially immersed for 4 days in aerated distilled water were covered with a greyish black film, and localized penetrative attack was apparent. On immersion in de-aerated distilled water the greyish-black film soon disappeared, leaving a light grey surface on which interference colours could be seen. The loops had not failed in 60 days, after which time air was bubbled through the water. Both loops failed in a further 7 days, i.e. after a total time of 11 days in aerated water.

Two loops which had been initially immersed for 10 days (one of which had just failed) in distilled water were covered with a uniform dark grey film, and the localized penetrative attack was apparent. On immersion in de-aerated distilled water streams of bubbles could be seen coming from isolated points on the surface. After a short time the dark grey film disappeared, leaving a light grey surface which did not show interference colours. The unfailed loop remained intact for 29 days, after which time air was bubbled through the water and the loop then failed after 2 hr., i.e. after a total of 10 days + 2 hr. in aerated water.

Microscopical examination of these loops showed that on all of them there was more of the localized penetrative attack than on the control specimens immersed in aerated water for 11 days only. The attack was deeper and the tips of the small cracks more rounded than on the control specimens.

The experiments described indicate that stress-corrosion was not taking place in de-aerated distilled water. Once localized penetrative attack has begun, however, the results suggest that it can proceed in de-aerated distilled water.

(h) *Stress-Corrosion in Solutions Other than Distilled Water.*

Stressed-loop tests were carried out in solutions of magnesium carbonate (saturated), 0.5% potassium fluoride, 0.5% potassium hydrogen fluoride, 0.5% hydrofluoric acid, and 0.05% potassium chromate on the magnesium-5% aluminium alloy (MWY3 sheet) in the as-received and solution-treated conditions. The results are shown in Table VI.

In distilled water and in saturated magnesium carbonate solution bubbles formed initially and the loops became covered with a black-grey film which was more uniform on those in the magnesium carbonate solution.

On immersing loops in 0.5% potassium fluoride solution rapid evolution of bubbles took place from isolated points on the surfaces. No black film was formed, and after 6 days the surface was bright except for a few areas covered with a dull white film.

TABLE VI.—*Stress-Corrosion Behaviour of Stressed Magnesium-5% Aluminium Alloy Loops in Various Solutions.*

Solution	pH	Individual Loop Life, days *	
		Solution-Treated	As-received
Distilled water	5.0 approx.	4, 5½, 5½ (5)	12, 14, 14 (13)
Saturated magnesium carbonate	9.4	4, 5½, 5½ (5)	9½, 9½, 14 (11)
0.5% Potassium fluoride	7.4	†	7, 6, 6 (6)
0.5% Potassium hydrogen fluoride	3.4	1½, 1½, 1½ (1½)	1, 1, 1 (1)
0.5% Hydrofluoric acid	n.d.	1, 1, 1, 1, 1 (1)	†
0.05% Potassium chromate	7.4	see text	see text

* Figures in brackets give mean life.

† Not tested. n.d. = not determined.

In 0.5% potassium hydrogen fluoride solution rapid effervescence occurred initially, gas bubbles coming from isolated parts of the surface, but this evolution of gas soon ceased. After approximately 2 hr. the specimens were covered with a golden brown film, which then quickly disappeared, and after 1 day the loops were quite bright. The loops cracked at this stage and gas was evolved from the crack. Since slight attack by the potassium hydrogen fluoride on the glass container might have had an effect on the stress-corrosion life, the experiment was repeated in a wax container, but the results were the same as before.

Loops immersed in 0.5% hydrofluoric acid behaved similarly to those in 0.5% potassium hydrogen fluoride solution, except that a greyish film was formed during corrosion and more general attack occurred than in the latter solution.

The loops in 0.05% potassium chromate solution slowly became covered with a black film, which was complete after approximately 6 days. Certain areas of the surface running perpendicular to the direction of stress had been attacked. The stress-corrosion cracks produced tended to follow these attacked areas.

Microscopical examination of the loops which had failed in distilled water and saturated magnesium carbonate solution revealed localized penetrative attack and the transcrystalline cracking as described earlier. The loops in 0.5% potassium fluoride, 0.5% potassium hydrogen fluoride solutions, and 0.5% hydrofluoric acid showed trans-

crystalline cracking but no localized penetrative attack. Loops immersed in 0.5% potassium hydrogen fluoride solution had a large number of deep cracks in addition to the main one, indicating that in this solution the tendency for one crack to outstrip the others had been reduced. This also occurs to some extent in distilled water (Figs. 5 and 6, Plate LXX).

Loops in 0.05% potassium chromate solution of $pH = 7.4$ (as-received, solution-treated, and solution-treated and aged) showed intercrystalline cracking with some transcrystalline branches. As in 0.5% potassium hydrogen fluoride solution, there were several cracks penetrating almost through the cross-section of the loop, as well as the main fracture. This made it difficult to assign a definite time of failure. In all conditions there was some intercrystalline corrosion present in the unstressed control specimens, both in the plastically deformed and other parts. Fig. 8 (Plate LXX) shows intercrystalline cracking in a stressed loop (as received) after 90 days' immersion.

A point of great interest is the demonstration that intercrystalline cracking can take place in an apparently homogeneous material and that in the same material transcrystalline and intercrystalline cracking can occur according to the solution used.

Mears, Brown, and Dix ¹⁰ have reported intercrystalline cracking of an alloy similar to the magnesium-6% aluminium-1% zinc alloy in a solution containing sodium chloride and potassium chromate. They found that the type of cracking was dependent on the pH of the solution, transcrystalline cracking occurring with pH of 8.1 and intercrystalline cracking with pH of 5.0. This relationship does not hold for the magnesium-5% aluminium alloy, since transcrystalline cracking was observed in various solutions with pH ranging from 3.4 to 9.4 (see Table VI).

(i) *Electrochemical Work.*

(1) *Potential Measurements on Solution-Treated Material, β Phase ($Mg_{17}Al_{12}$), and Iron in Various Solutions.*—Electrode potentials of solution-treated magnesium-5% aluminium alloy, the β phase (cast to the composition $Mg_{17}Al_{12}$), and pure iron were measured in the following solutions: (i) distilled water, (ii) saturated magnesium carbonate, (iii) 0.05% sodium chloride, (iv) 0.1% sodium chloride, (v) 0.05% potassium chromate, and (vi) 0.5% potassium fluoride. The potentials were measured against an *N*-calomel half-cell using a Cambridge pH meter. All specimens were prepared in the same way as described for the loops, except that the iron was emiered. The steady potentials (against *N*-calomel electrode) are given in Table VII.

In all the solutions the β phase and iron are cathodic to the solid solution.

On scratching the solid-solution and β electrodes the potentials became more anodic and the electrodes rapidly reformed when scratching ceased, except in 0.5% potassium fluoride solution when longer times were needed for film re-formation. On scratching the iron electrodes very little change in potential occurred except in 0.05% potassium chromate solution, where the potential became more anodic and film re-formation occurred when scratching ceased. These results indicate that in all the solutions corrosion films were formed on the solid-solution and β electrodes, whilst on the iron electrodes only in 0.05% potassium chromate solution was the film at all protective.

TABLE VII.—*Electrode Potentials of Magnesium-5% Aluminium Alloy (MWY3 Sheet), β Phase ($Mg_{17}Al_{12}$), and Iron in Various Solutions.*

Solution	Steady Potential, V.		
	Solution-Treated Mg-5% Al Alloy	$Mg_{17}Al_{12}$	Pure Fe
Distilled water	-1.26 *	-0.95	-0.75
Saturated magnesium carbonate	-1.61	-1.00	-0.52
0.5% Potassium fluoride	-1.33	-1.20	-0.74
0.05% Sodium chloride	-1.48	-1.30	N
0.1% Sodium chloride	-1.50	-1.10	N
0.05% Potassium chromate.	-1.64	-1.10	-0.18

N = Not measured.

* MWY1 sheet, MWY3 sheet gave -1.40V.

(2) *Potential Measurements on Stressed Loops.*—Potential/time curves for a stressed loop made from MWY3 in the as-received condition, and an unstressed piece of the same material in 0.5% potassium hydrogen fluoride solution were automatically recorded. The first 6 hr. of the record for the stressed loop (Fig. 13) shows that the corrosion film appeared to be continually breaking down and re-forming. Later the potential became more cathodic, reaching -0.6 V. (N-calomel) in 14 hr., with fluctuations similar to those shown in Fig. 13, but of smaller amplitude still occurring. After 20 hr. there was a sudden change in the potential to a value of about -1.04 V.; this was probably due to exposure of bare metal by cracking, a crack being visible after 24 hr. The initial part of the potential/time curve for the unstressed specimen (Fig. 14) shows that even in the absence of applied stress the film appears to be continually breaking down and re-forming, though by no means to the same extent as on the stressed loop.

Potential/time curves for stressed loops in 0.5% potassium fluoride solution with and without passage of air were also automatically recorded. The potential of the loop in the stagnant solution changed

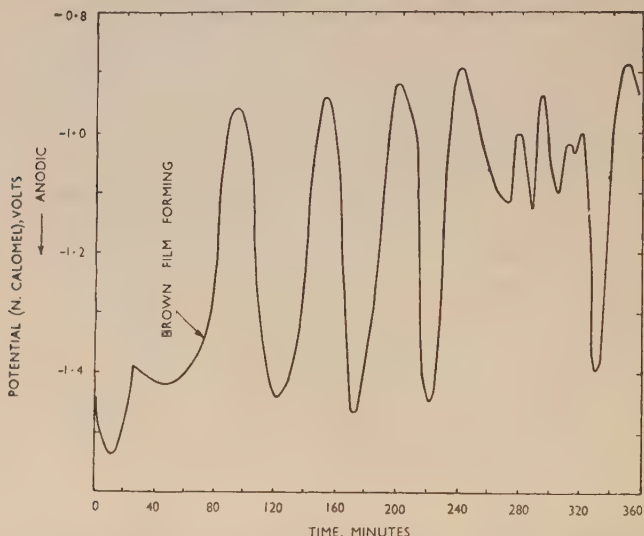


FIG. 13.—Potential/Time Curve for Stressed Magnesium-5% Aluminium Alloy Loop (As-Received) in 0.5% Potassium Hydrogen Fluoride Solution.

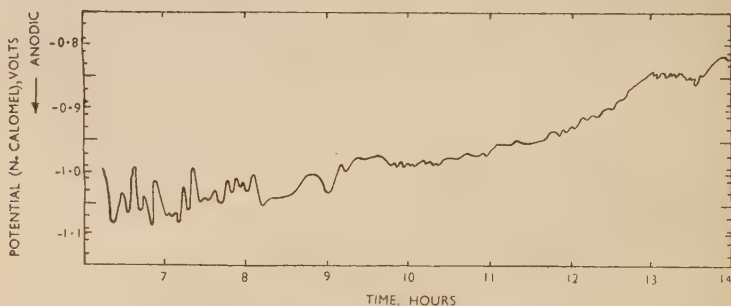


FIG. 14.—Potential/Time Curve for Unstressed Magnesium-5% Aluminium Alloy (As-Received) in 0.5% Potassium Hydrogen Fluoride Solution.

from -1.8 to -1.0 V. in approximately 20 hr., after which further change was very slight. The potential was never steady, similar but smaller fluctuations to those shown in Fig. 13 occurring. The loop failed in 7 days. The potential of the loop in the aerated solution changed from -1.8 to -1.56 V. in 20 hr., and thereafter remained perfectly steady. This loop failed in 11 days.

These results suggest that there is a close connection between the stress-corrosion susceptibility and the properties of the surface film, rapid failures being associated with unstable films. The results in 0.5% potassium hydrogen fluoride solution indicate that applied stress has the effect of cracking surface films, or enhancing a cracking tendency that is present in the absence of applied stress.

3. *Corrosion of Magnesium and Magnesium Alloys in Distilled Water.*

To compare the behaviour of various magnesium-base materials with magnesium-5% aluminium alloy, polished microspecimens of high-purity magnesium, commercially pure magnesium, magnesium-1.5% manganese alloy, and cast magnesium-8% aluminium alloy were immersed in distilled water for periods up to 60 days, and examined periodically under the microscope. Finally, the specimens were sectioned at right angles to the surface to examine the inward penetration of corrosion. No localized penetrative attack occurred in the super-purity magnesium or in the magnesium-manganese alloy. There were a few areas of such attack in the commercial purity magnesium, although it was not very deep. In the cast magnesium-8% aluminium alloy corrosion was concentrated on areas of solid solution approximately midway between islands of the β phase which remained bright and unattacked. The corroded portions showed localized penetrative attack similar to that taking place in the wrought magnesium-5% aluminium alloy, though not developed to the same extent.

4. *Stress-Corrosion of Magnesium Alloys and High-Purity Magnesium in Distilled Water and 0.5% Potassium Hydrogen Fluoride Solution.*

(a) *Loop Tests.*

Stressed-loop tests were carried out on magnesium-2% manganese-0.5% cerium, magnesium-3% aluminium-1% zinc, magnesium-3% aluminium, and magnesium-3% zinc-0.7% zirconium alloys in distilled water and 0.5% potassium hydrogen fluoride solution. All materials were tested in the as-received condition (i.e. annealed). The results are given in Table VIII.

In addition, two loops made from magnesium-2% manganese alloy failed in 35 days in 0.5% potassium hydrogen fluoride solution. These results are not directly comparable with the others, as owing to the very low elongation of this material it was necessary to make the loops with larger radius. Cracking was transcrystalline in all alloys except the magnesium-3% zinc-0.7% zirconium alloy in which it was intercrystalline. Figs. 9 and 10 (Plate LXXI) show stress-corrosion

TABLE VIII.—*Stress-Corrosion Loop Tests on Commercial Alloys in Distilled Water and 0.5% Potassium Hydrogen Fluoride Solution.*

Alloy	Distilled Water		0.5% Potassium Hydrogen Fluoride	
	Loop Life, days *			
	Unchromated	Chromated	Unchromated	Chromated
Magnesium-2% manganese-0.5% cerium	23, 25 (24)	5½, 5½ (5½)	6, 7, 5 (6)	2, 2, 2 (2)
Magnesium-3% aluminium-1% zinc	3, 3, 3 (3)	3, 3, 3 (3)	1, 2, 7 (3)	8, 8, 8 (8)
Magnesium-3% aluminium	5½, 5½, 5½ (5½)	5½, 11, 5½ (7)	5, 7, 8 (7)	8, 8, 8 (8)
Magnesium-3% zinc-0.7% zirconium	33, 56, 70 (53)	†	4, 4, 4 (4)	†

N.B.—All materials 16 S.W.G. except magnesium-3% zinc-0.7% zirconium alloy which was 18 S.W.G.

* Figures in brackets give mean life.

† Not tested.

cracks in the magnesium-2% manganese and magnesium-3% zinc-0.7% zirconium alloys, respectively, after immersion in 0.5% potassium hydrogen fluoride solution.

All loops tested in 0.5% potassium hydrogen fluoride solution, except those of magnesium-2% manganese and magnesium-2% manganese-0.5% cerium alloy, showed many deep cracks besides the main crack (see Fig. 11, Plate LXXI).

(b) *Direct-Tensile Stress-Corrosion Tests.*

Direct-tensile stress-corrosion tests were carried out on fully annealed high-purity magnesium and annealed commercial-purity magnesium-2% manganese alloy partially immersed in 0.5% potassium hydrogen fluoride solution. The results are given in Table IX.

TABLE IX.—*Stress-Corrosion Tests on High-Purity Magnesium and Commercial-Purity Magnesium-2% Manganese Alloy in 0.5% Potassium Hydrogen Fluoride Solution.*

Material	Mechanical Properties Perpendicular to Rolling Direction			Initial Applied Stress, tons/in. ²	Stress-Corrosion life, days
	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation on 2 in., %		
High-purity magnesium	13.7	5.0	7	7 5 4	1½, 1½ 1½, 2, 3 5, 6
Magnesium-2% manganese alloy	16.7	8.6	12	7 5	6 24, 38

Unstressed control specimens showed no loss of strength or elongation.

Microscopical examination showed that the cracking in both materials was transcrystalline. The main difference was that in the magnesium-2% manganese alloy there was only one crack with associated branches, whilst in the high-purity magnesium there were many cracks in addition to the main one; Fig. 12 (Plate LXXI) shows one of these subsidiary cracks. It is clear from Fig. 12 that there is no tendency for the crack to follow either grain or twin boundaries.

IV.—SUMMARY OF RESULTS.

The results show that magnesium-5% aluminium alloy (whether chromated or not) under certain corrosive conditions tends to undergo a localized penetrative type of transcrystalline corrosion, irrespective of its metallurgical condition. This has also been observed to a much smaller extent in commercial-purity magnesium and in a cast magnesium alloy containing 8% aluminium. The presence of oxygen is necessary for it to occur in distilled water. This type of corrosion is more marked with higher iron content and increases with the degree of plastic deformation. The imposition of stress causes the rapid advancement of certain isolated "cracks" initiated by this type of corrosion, giving transcrystalline stress-corrosion cracks which have no apparent relation to the metallographic structure of the material. Stress-corrosion susceptibility has been found to increase with the iron content and with elastic deformation and to decrease with the precipitation of the β phase $Mg_{17}Al_{12}$. In the absence of oxygen stress-corrosion is prevented, or at least greatly retarded.

Magnesium-2% manganese-0.5% cerium, magnesium-3% aluminium, magnesium-3% aluminium-1% zinc and magnesium-6% aluminium-1% zinc alloys have also been found susceptible to stress-corrosion in distilled water, giving transcrystalline cracks. In addition to the above mentioned alloys, high-purity magnesium, magnesium-5% aluminium and magnesium-2% manganese alloys were found to crack in a transcrystalline manner when stressed in 0.5% potassium hydrogen fluoride solution.

Intercrystalline cracking of magnesium-5% aluminium alloy occurred in 0.05% potassium chromate solution, and of magnesium-3% zinc-0.7% zirconium alloy in distilled water and 0.5% potassium hydrogen fluoride solution.

V.—DISCUSSION OF RESULTS.

It seems likely that some common factor operates in the stress-corrosion cracking of the seven magnesium-base alloys tested. Cracking is apparently not due to the presence of a second phase associated with the alloy system, since cracking can occur (a) in solution-treated

material, and (b) in high-purity magnesium. Cracking may therefore be associated with the minor impurities which are known to have deleterious effects on the ordinary corrosion-resistance.

Many investigators have shown that iron plays an important part in the corrosion of magnesium and its alloys. Hanawalt¹⁶ and his collaborators proved that there exists a tolerance limit for iron (of about 0.017%), below which the rate of corrosion of magnesium is small, and above which the corrosion rate increases rapidly with iron content. Aluminium was found to decrease the tolerance limit of iron (e.g. 7% aluminium decreased it to approximately 0.0007%). The same workers confirmed by microscopical examination that with a constant iron content there were more iron particles in magnesium-3% aluminium alloy than in unalloyed magnesium. Also these iron particles were found to segregate in varying degree throughout the samples. The effect of iron has also been studied by Heidenreich⁷ and his collaborators by means of the electron microscope. By using a special etching technique, electron micrographs of the magnesium-aluminium solid solution were obtained showing a considerable etch structure which was absent in the case of pure magnesium. All likely causes of this structure were eliminated except the effect of the iron impurity. It was also found that the presence of aluminium as well as iron was necessary for the formation of this structure. The authors concluded that the fine structure represented the distribution of iron or iron-aluminium compounds segregated between mosaic blocks in the crystal. It is interesting to note that when the alloy was heat-treated in such a way that a large amount of the second phase was precipitated, the fine structure practically disappeared, indicating that the iron-aluminium compound is more soluble in the β phase ($\text{Mg}_{17}\text{Al}_{12}$). This was confirmed by direct experiment.

It has been found in the present work that the tendency to undergo localized penetrative attack and the stress-corrosion susceptibility of magnesium-5% aluminium both increased as the iron content was raised from 0.0019% to 0.013%, and were both diminished by the presence of $\text{Mg}_{17}\text{Al}_{12}$. This suggests that there is a close connection between the fine dispersion of the iron or iron-aluminium compound described by Heidenreich and the stress-corrosion properties. If, as suggested, iron impurities are responsible for stress-corrosion failure in the magnesium-base materials, it is obvious that very small amounts of iron are effective, e.g. 0.0019% in magnesium-5% aluminium and 0.004% in high-purity magnesium.

No detailed mechanism of the stress-corrosion of magnesium alloys can be put forward at this stage, but it is certain that the mechanism

is in part electrochemical. This is shown by the necessity for the presence of dissolved oxygen for the occurrence of cracking and also by the very dissimilar effects observed in different electrolytes. Of particular interest is the fact that cracking of magnesium-5% aluminium alloy is intercrystalline or transcrystalline according to the solution used. This is presumably due to a different distribution of the local anodes and cathodes in the different solutions. It may be significant that iron immersed in the solution causing intercrystalline cracking of magnesium-5% aluminium alloy (0.05% potassium chromate) became highly cathodic owing to film formation.

All the magnesium alloys tested have been found susceptible to stress-corrosion in distilled water or 0.5% potassium hydrogen fluoride solution. However, some of the alloys are known to be reliable in engineering service, and it therefore seems desirable to comment upon the practical implications of the results. Extensive service experience has shown that the magnesium-6% aluminium-1% zinc alloy is prone to stress-corrosion failure, and in the U.S.A. it has been largely replaced for sheet by a lower-strength magnesium-3% aluminium-1% zinc alloy, and in Germany by the magnesium-2% manganese-0.5% cerium alloy. (The alloy containing 6% aluminium has been little used in this country, largely on grounds of rolling difficulty.) The present results confirm the wisdom of the German change of alloy in so far as the magnesium-2% manganese-0.5% cerium sheet had a comparatively long stress-corrosion life in distilled water. The magnesium-1.5% manganese alloy has been, and still is, used extensively in both Europe and America and it is generally accepted to be immune from stress-corrosion failure. The present results suggest that this alloy is superior to those containing aluminium, for when tested at about the 0.1% proof stress in the very active 0.5% potassium hydrogen fluoride solution the stress-corrosion life was of the same order as that obtained by stressing the magnesium-5% aluminium alloy in the much less active distilled water.

In practice magnesium is used for holding hydrofluoric acid and fluoride solutions, but the concentrations of the solutions are kept above a certain limit to avoid excessive general corrosion which might otherwise occur; the present results show that very dilute solutions could cause failure by stress-corrosion. It is understood from the manufacturers²⁰ that the magnesium-3% zinc-0.7% zirconium alloy sheet has shown virtually complete freedom from stress-corrosion tendencies under long-term atmospheric exposure and in total immersion or spray tests using 3% sodium chloride. The present results show that the stress-corrosion life of the zirconium-containing sheet is

similar to magnesium-2% manganese-0.5% cerium and magnesium-3% aluminium-1% zinc sheet in 0.5% potassium hydrogen fluoride, but in distilled water its stress-corrosion resistance is superior to that of the magnesium-2% manganese-0.5% cerium alloy and of an altogether higher order than that of the magnesium-3% aluminium-1% zinc alloy (which may, however, not be entirely representative of current American production).

Note Added in Proof.—Since this work was submitted for publication, a paper on the stress-corrosion properties of magnesium alloys has been published in America by Logan and Hessing,²¹ whose results agree well with those published here.

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THE MANIPULATION AND TEMPERATURE CALIBRATION OF HIGH-TEMPERATURE DEBYE-SCHERRER X-RAY CAMERAS.* 1292

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SYNOPSIS.

Critical experiments designed to test the temperature distribution in the gap between the furnaces of a Unicam high-temperature Debye-Scherrer X-ray camera are described. Consideration is also given to the reliability of the internal calibration of the measuring thermocouple in terms of the lattice spacings of a standard substance at various temperatures. It is concluded that no method involving moving thermocouples is entirely satisfactory for exploring the temperature distribution in the furnace gap, or for finding the specimen temperature. A reliable method for determining temperature gradients in the specimen has been developed, involving the attachment of fine thermocouples in given positions to copper wires, which are mounted in the position actually occupied by the specimen. Measurements made by this method, when adequate precautions are taken, agree well with X-ray determinations of the mean specimen temperature over the irradiated length; the necessary precautions are discussed in detail. The circuits used for the control of furnace temperature ($\pm 0.4^\circ \text{C.}$), and for adjusting the temperatures of the upper and lower furnaces to equality within $\pm 0.1^\circ \text{C.}$, are also described.

Experiments on internal calibration against the lattice spacings of pure silver show clearly that the emissivities of the standard and experimental specimens should be as nearly as possible identical. If calibration experiments are carried out using a bright specimen, and experiments are subsequently carried out with specimens of higher emissivity, errors up to 20°C. may occur in the assessment of the specimen temperature at 500°C. This source of error has not previously been discussed, and merits careful attention in future work.

I.—INTRODUCTION.

For many problems, such as crystal-structure determinations of phases which decompose on quenching, the temperatures of the specimens used in high-temperature Debye-Scherrer cameras need not be known to a very high degree of accuracy. In other cases, such as the investigation of superlattice limits, thermal expansion, and exact transformation temperatures, both the specimen temperature and the thermal gradients in the specimen must be accurately known. With the high-temperature cameras currently available commercially, these conditions are difficult

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to meet. The authors have recently concluded a calibration of a Unicam high-temperature camera, and have carried out an exploration of the temperature distribution in the specimen, no facilities for which exist with the instrument as supplied. Since this work revealed sources of error which might be undetected in routine use, a description of the experiments and the technique finally perfected may be of interest to others handling this equipment, which is becoming increasingly used in metallurgical laboratories.

II.—TYPE OF INSTRUMENT AND GENERAL DESIDERATA.

The instrument, a cylindrical camera with detachable film-carrier, is shown diagrammatically in Fig. 1; it includes a heating chamber

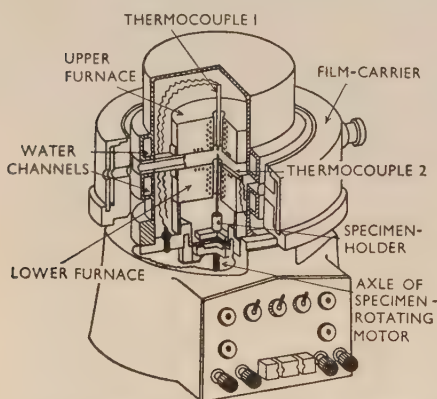


FIG. 1.—High-Temperature X-Ray Camera.

formed by two cylindrical resistance-wound furnaces placed vertically one above the other. Radiation enters and leaves the chamber by a 7-mm. gap between the furnaces. The specimen projects axially into the heating chamber from a rotatable holder situated in the water-cooled camera base. Two platinum/platinum-rhodium thermocouples are supplied; one projects from the top of the upper furnace into the

camera, and is adjustable along the camera axis, while the other is cemented horizontally to the upper surface of the lower furnace unit, the tip projecting slightly into the central heated space. The adjustable thermocouple, though coaxial with the specimen, can only be placed near the centre of the heating chamber, in the position which a specimen would occupy, in the absence of the specimen. The thermocouple wires are led to sockets, on the cool part of the camera, into which compensating leads are plugged to connect the thermocouples, via cold junctions in melting ice if desired, to suitable measuring instruments. As supplied, the two thermocouples cannot be used simultaneously. Difficulty was also experienced in arranging equality of temperature in the two furnaces, and in reproducing temperatures, as measured potentiometrically by the thermocouples provided, from day to day, without altering the furnace rheostat settings. Further,

no sufficiently accurate estimation of temperature gradients in the specimen was possible. It was decided to explore these features, bearing in mind the following general desiderata :

- (i) That the temperature of the specimen should be accurately maintained over long periods.
- (ii) That this temperature should be accurately measurable.
- (iii) That the gradients in the specimen should be small and accurately measurable.

III.—EXPLORATORY EXPERIMENTS.

For initial experiments, the horizontal thermocouple No. 2, being firmly fixed relative to the furnaces, was used as a reference, to which all other measured temperatures were related. It was subsequently calibrated *in situ* against the lattice spacings of pure silver at various temperatures (see Section VI). Thermocouple No. 1 (Fig. 2) was replaced by an Alumel/Chromel thermocouple made of thin wire (0.005 in. dia.) to diminish conduction from the tip, with which it was intended to explore the temperature distribution in the furnace gap, with particular reference to the central 5 mm. which, from measurement of the collimator system, corresponded with the irradiated length of specimen. The temperature distribution depends upon heat losses through the gap to the surroundings, and also upon the relative temperatures of the upper and lower furnaces; these temperatures should be equal, and it was intended to ensure this by measurements taken with the exploring thermocouple just within the mouths of the respective furnaces. During the experiments, the overall furnace temperature was controlled by means of an Ether-Wheelco temperature regulator working from thermocouple No. 2.

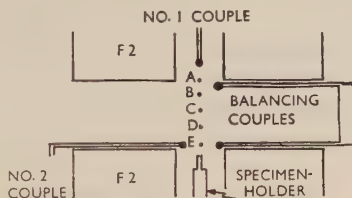


FIG. 2.—Thermocouple Positions.

1. Measurements Made in the Absence of the Specimen.

With the exploring thermocouple, measurements were made at *A*, *B*, *C*, *D*, and *E* (Fig. 2). The camera was not evacuated. The apparent temperature distribution observed was unsymmetrical about *C* and not reproducible; it was found difficult, by rheostat adjustments, to reduce the temperature of the upper furnace (measured at *A*) to the temperature observed at *E*. Part of the irreproducibility was due to small lateral displacements of the thermocouple tip. This was

eliminated by fitting an axial Pyrex guide tube, and convection currents were avoided by evacuating the camera continuously. The temperature determinations at the five points, at a given temperature, were still not reproducible. The apparent equality of the measured temperatures of the upper and lower furnaces proved to be affected by the passage of the exploring thermocouple from position to position, owing to variable conduction effects from the thermocouple tip down the wires or the reverse, so that it was necessary to adjust this balance independently of the exploring thermocouple. This was done by a differential-thermocouple device, described below. It was now found that, with the furnaces at the same temperature, as indicated by this device, the exploring thermocouple indicated that the upper furnace was the hotter. Thus, with the tip at *A*, heat was conducted to it from the hot zone of the upper furnace, while, with the tip at *E*, heat was conducted away from it because the leads immediately behind the tip were in the cooler gap. Apparent temperatures at *A* were therefore too high and those at *E* too low. The use of a single exploring thermocouple, though frequently suggested, is fundamentally unsound; relative temperatures in the gap must be measured with thermocouples whose leads are subject to similar thermal conditions whatever the tip positions.

Accordingly, the gap was further explored with two identical axial thermocouples, projecting respectively from the upper and lower furnaces. Under these conditions, when the tips were situated symmetrically about *C*, or touching at *C*, and the furnaces adjusted to give equal readings for each thermocouple, the differential-thermocouple device also indicated no temperature difference between the furnaces. Measurements of the temperature at *A*, *B*, *C*, *D*, and *E* were, however, again not reproducible. Experiments showed that thermal e.m.f.'s arising at the junctions of the thermocouples with their compensating leads on the camera base were contributing to the irreproducibility. All compensating leads were therefore eliminated and the thermocouple wires themselves extended to the cold-junction box at the temperature of melting ice. With the improved reproducibility obtained, it was found that conduction down the thermocouple wires, which varied according to tip position, was magnifying the gradient. The use of movable exploring thermocouples was therefore abandoned.

2. *Measurements Using Dummy Specimen Wires with Attached Thermocouples.*

In view of the difficulties described, the method finally selected for examination was to seal fine 0.005-in.-dia. Alumel/Chromel thermo-

couples symmetrically in pairs to copper wires of 0.5 mm. dia., so that when the wires were mounted and centred in the specimen-holder, the thermocouple tips were in positions *A* and *E*, or *B* and *D*. For the position *C*, wires with a single central thermocouple were used. This method had the advantage of reproducing subsequent experimental conditions adequately. The fine thermocouples were silver-soldered to the copper wires; tests proved that this soldering process did not affect the e.m.f./temperature characteristics of the thermocouples. Experiments with this arrangement showed that the measured temperatures were independent of degree of vacuum, of small variations in the lateral position of the copper wire, and of the positions of the thermocouple leads which lay in the gap between the furnaces. It is important to note that, with this arrangement, the thermocouple wires do not pass through either of the furnace hot zones, and the thermal path of the leads is to a great extent the same for each position of the tip. For good reproducibility, however, it was necessary to standardize the position of thermocouple No. 1, which was used in this series of experiments to activate the temperature regulator, and to minimize heat conduction down the specimen to the cool specimen-holder by interposing a silica-rod heat insulator between the specimen and the holder. A final refinement found to be needed was to arrange that the copper wire was symmetrically situated about the mid-point *C*, with the lengths projecting into the upper and lower furnaces exactly equal. Taking all the precautions mentioned above, it was found that the temperature distribution was symmetrical about *C*; and that it was possible to determine the temperature gradients between *A* and *E* accurately in the range 250°–550° C., which was the range of temperature of interest for a specific problem. The determinations could be repeated on several different occasions with a reproducibility of within $\pm 1.5^\circ$ C. To minimize any remaining conduction effects, the final measurements were made with one thermocouple only, soldered to the copper wire in each of the standard positions.

IV.—FINAL EXPERIMENTAL ARRANGEMENTS.

The arrangement of the furnaces, measuring thermocouple (No. 2) and specimen, or copper wire with attached thermocouple, was maintained exactly as described above; after some experience, other experimental arrangements were standardized in the following manner.

1. *Furnace-Balancing Device.*

As emphasized above, equality of temperature in the upper and lower furnaces is essential. In order to be able to adjust this quickly

and accurately, two identical Alumel/Chromel thermocouples (wires 0.0200 in. in dia.), with their e.m.f.'s opposed, were mounted rigidly as indicated in Fig. 2, and in Fig. 3, which shows the circuit used. The opposed thermocouples were connected to a sensitive galvanometer,

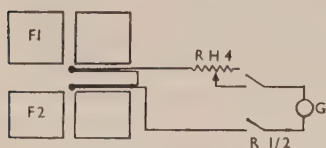


FIG. 3.—Furnace-Balance Indicator Circuit.

used with a lamp and scale, via a switch, a variable resistance $RH4$, and a relay $R1$. On heating or cooling, the two furnaces approach equilibrium at different rates; this necessitates the use of $RH4$ to decrease the sensitivity of the galvanometer. $R1$ is operated elec-

trically on failure of the current supply to one or both of the furnaces. The furnace rheostats can then be adjusted manually to give a null galvanometer reading corresponding to equality of temperature within $\pm 0.1^\circ \text{C}$. As stated above, adjustment by this method agreed exactly with adjustment using the gradient-determining thermocouples.

2. Control Technique.

Using the camera as supplied and an Ether-Wheelco temperature regulator, the accuracy of temperature control was $\pm 3.0^\circ \text{C}$., while a long-period drift of $\pm 5.0^\circ \text{C}$. was noted. This could not be tolerated. The controller utilizes the change of inductance between two coils as a metallic "flag" attached to the end of a millivoltmeter needle enters, or withdraws from, the space between them; the sensitivity when the instrument is correctly adjusted depends on the e.m.f./temperature characteristics of the controlling thermocouple and on the deflection characteristics of the millivoltmeter. Sensitivity was increased ten-fold by removing from the controller a 75Ω series resistance and substituting an Alumel/Chromel thermocouple for the noble-metal thermocouple No. 1; this thermocouple was placed close to the upper furnace wall to avoid thermal lag.

Full-scale deflection of the millivoltmeter then corresponded to approximately 140°C . For higher temperatures, part of the e.m.f. of the controlling thermocouple was balanced potentiometrically, the remainder being applied to the controller. The circuit employed is shown in Fig. 4.

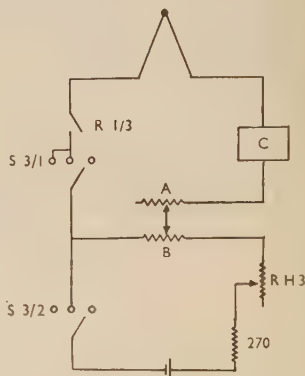


FIG. 4.—Control Circuit.

Resistances *A* and *B* were arranged so that the resistance in the thermocouple circuit remained constant. A wafer switch *S3* ensured that the thermocouple circuit was closed and the battery circuit open ($<140^{\circ}$ C.), or both circuits were opened or closed simultaneously ($>140^{\circ}$ C.). The fine rheostat *RH3* provides fine control of the potential supplied by the battery, and allows a 22° C. range of fine adjustment of temperature. It is used only to correct any small drifts detected by thermocouple No. 2. Stability of control depends on the e.m.f. of the battery (slow-discharge Exide accumulator DFG); to minimize variations in this, the battery was housed in a thermally insulated box remote from the X-ray cubicle, inside which slow temperature drifts were liable to occur during an exposure. With the battery thus protected against temperature variations, furnace temperatures were reproducible from day to day to within $\pm 0.5^{\circ}$ C. without alteration of rheostats *A* and *B*, or the control point of the regulator. This is an indication of the reliability of the circuit employed. To operate the control, the furnace temperature is adjusted close to that required, using thermocouple No. 2 as an indicator; the control circuit is then switched in, and the resistance *B* adjusted to bring the controller millivoltmeter needle slightly below its control point. Rheostat *RH3* is now set at its mid-point, and resistance *A* adjusted to the same reading as *B*. Using thermocouple 2, the readings at which the controller now operates are noted, and the setting of the control point on the regulator is adjusted until these readings bracket the desired temperature. The resistances in the furnace circuits are now adjusted so that the heating and cooling periods are equal. Under these conditions, and using a mains' supply stabilized by an electronic device constructed by Mr. Williamson of the Metallurgy Department, Birmingham University, who will publish details later, control to within $\pm 0.4^{\circ}$ C. of the desired temperature over long periods was obtainable.

3. *Main Circuit.*

Fig. 5 illustrates the main circuit for the furnace and specimen-rotating motor units. *F1* and *F2* are the upper and lower furnaces, with series resistances *RH1* and *RH2*, and *M1* is the motor. On the right of the diagram appears the rectifier used to operate the safety relay shown as *R1/2* and *R1/3* in Figs. 3 and 4. It is clear that a safety device is required to prevent damage to the galvanometer in the balancing circuit (Fig. 3) should one furnace cool unexpectedly, and to the controller millivoltmeter should either or both of the furnaces cool unexpectedly, owing to furnace failure, fuses blowing, or mains' failure.

The current passing through the relay circuit is adjusted, with the aid of the rheostat *RH5* shown in Fig. 5, so that the relay just remains closed under normal conditions; if the mains' voltage falls by 20%, both the balancing circuit and the controller thermocouple circuit are

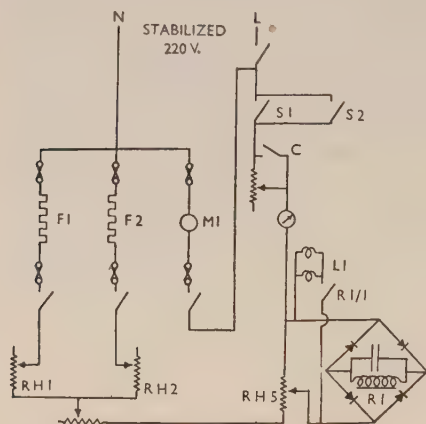


FIG. 5.—Furnace and Specimen Motor Circuit.

opened. Similarly, these circuits are opened if either *F1* or *F2* fail, since the current passing through the relay circuit falls below the operating limit. Damage to the camera results if the water supply to the cooling chambers fails; a simple water relay is therefore included in the furnace circuits, which are opened on water failure. This action also operates the safety relay *R1*, which, as shown in Fig. 5, is included in a signal light circuit so that, when an accident occurs, indicator lights both inside and outside the X-ray machine cubicle are extinguished.

An auxiliary circuit is used to drive the pump for camera evacuation, and to provide power, through transformers, for galvanometer lights, &c.

V.—MEASUREMENT OF TEMPERATURE GRADIENTS IN FURNACE GAP.

For the temperature-distribution measurements, the camera was accurately controlled at various temperatures using thermocouple 1 in a fixed position, and the upper and lower furnaces were exactly equal in temperature. Thermocouple 2 was employed as reference thermocouple. The results obtained are summarized in Fig. 6, which gives the temperatures measured at *A*, *B*, *C*, *D*, and *E*, by thermocouples silver-soldered to copper wires as described above, for constant temperatures of 200°, 307°, 426°, and 541° C. as measured by thermocouple 2. In all cases the temperature at first falls on moving towards the centre *C*, and then rises to a maximum at the exact centre. The extreme temperature ranges are $\pm 2.25^\circ$, $\pm 2.5^\circ$, $\pm 3.75^\circ$, and $\pm 5.5^\circ$ C. at 200°, 307°, 426°, and 541° C., respectively; these figures were accurately reproducible, but could not be improved with the present camera. The 7-mm. gap between the upper and lower furnace units is considered

to be excessive, and a better temperature distribution would result from a narrower gap. It is not the purpose of the present paper, however, to discuss the furnace design; although different designs may lead to appreciable modification of the temperature distribution, the measurement of the gradients requires the use of a method such as that

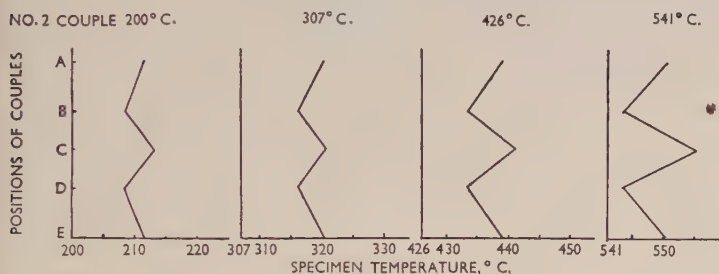


FIG. 6.—Specimen Temperature Distribution.

described here. It is important to note that measurement of the temperature difference between *A* or *E* and *C* (the so-called “centre-point correction”) does not give a true estimate of the temperature distribution in the specimen; further, thermocouple measurement of the temperature at *C* does not correspond with the average temperature of the specimen over its irradiated length.

VI.—TEMPERATURE CALIBRATION, AND INFLUENCE OF SURFACE CONDITION OF SPECIMEN.

The experiments carried out using thermocouples to explore the temperature distribution in the furnace gap indicate clearly that such temperature readings are quite unreliable as a guide to the specimen temperature, unless the measuring thermocouples are actually attached to the “specimen”, as in the final method for gradient determination adopted here. Calibration of a reference thermocouple (e.g. thermocouple 2) in terms of the lattice spacings of a standard substance whose lattice spacing/temperature characteristics are accurately known is therefore preferable. From the measured lattice spacing, the mean temperature of the standard specimen over its irradiated length (T_1) is calculated, and compared with the temperature indicated by the reference thermocouple (T_2). It is then assumed that, in subsequent experiments, the temperature of the specimen is T_1 if the reference thermocouple indicates temperature T_2 . Factors affecting this assumption were examined by a series of calibrations, using pure silver as a

standard substance; it was also of interest to compare the previous information with regard to temperature distributions in the specimen with the results obtained. The lattice spacings of silver at temperatures within the range of interest to the present work are accurately known from the work of Hume-Rothery and Reynolds;¹ although these were determined using thermocouple measurement of specimen temperature, and may be subject to some error from this cause, they agree well with macroscopic determinations in the range over which comparison may be made.

Duplicate exposures of bright silver-wire specimens were made at 200°, 300°, 400°, and 500° C.

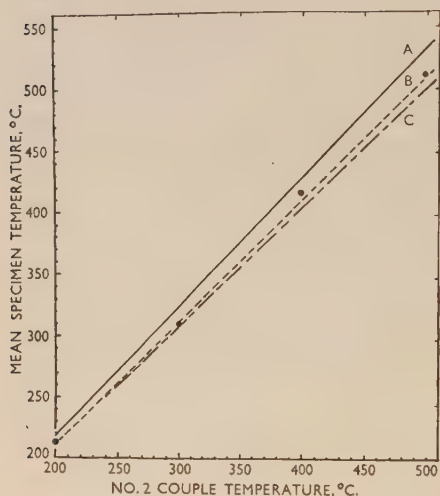


FIG. 7.—Calibration Curves.

KEY.

- A Bright silver (X-ray measurement).
- Black
- B Oxidized copper (thermocouple measurement).
- C Black

as measured by thermocouple 2, and the mean specimen temperatures over the irradiated lengths deduced are plotted against the temperature of thermocouple 2 in curve A of Fig. 7. Duplicate determinations agreed to within 3° C. The difference between mean specimen temperature and reference thermocouple readings is approximately 18° C. at 200° C., rising to 30° C. at 500° C. In order to determine the influence of specimen surface condition (i.e. emissivity properties) on the calibration, the experiments were repeated using a silver-wire

specimen coated with a colloidal graphite suspension and dried. The mean specimen temperatures calculated for given readings of thermocouple 2 were in all cases considerably lower than with the bright specimen, the difference between bright and black specimens increasing from 8° C. at 200° C. to 22° C. at 500° C. These results are plotted as the black circles in Fig. 7. These experiments emphasize a serious source of error which, to the authors' knowledge, has not been previously discussed; for accurate work, the emissivity characteristics of the standard calibration specimen and the experimental specimens must be as nearly as possible identical. This source

of error would be expected to be present in all cameras in which the upper and lower heaters are separated by a gap, although the magnitude of the error will clearly depend upon the details of the design.

The temperature deduced from lattice-spacing measurements is the mean specimen temperature over the irradiated length. This should agree with the mean specimen temperature calculated from the data of Fig. 6, provided the effective specimen length is known. The estimate of 5 mm. for the irradiated length was confirmed by exposing a strip of X-ray film held vertically in the specimen position, which, after development, showed a darkened area of length 4.5 mm. Considering a 5-mm. beam, mean specimen temperatures were calculated from Fig. 6, and plotted against the corresponding readings of thermocouple 2 to give curve B of Fig. 7, in excellent agreement with the points for blackened silver. The copper specimen used in the experiments summarized in Fig. 6 was in a surface-oxidized condition. Repetition of thermocouple-gradient measurements using a heavily blackened copper specimen gave the results plotted as curve C of Fig. 7; this curve falls only 6° C. below curve B at 500° C., the difference decreasing with falling temperature. The general agreement between the thermocouple measurements for the two copper specimens and the X-ray measurements for blackened silver may be regarded as satisfactory, when allowance is made for the difficulty introduced by the different emissivities of the specimens. It will also be appreciated that if the intensity of the X-ray beam is less towards its upper and lower limits than in the centre, the central portions of the specimen will contribute more heavily to the diffraction pattern than the top and bottom of the irradiated portion, so that the effective specimen length will be reduced. This would have the effect of raising the mean temperatures calculated from the thermocouple measurements by 4°–5° C., giving still closer agreement with the X-ray measurements on blackened silver.

To examine the effect of height of specimen irradiated, and the consistency of X-ray temperature calibrations with the thermocouple measurements, a blackened silver specimen was exposed at 500° C. (indicated by thermocouple 2), using a central beam collimated to a height of 1 mm. only. This was obtained by interposing, between the existing collimator and the specimen, a small brass plate bored with a millimetre hole, and thermally insulated from the top and bottom furnaces and from the specimen. The interference with the thermal conditions applying to the previous work was therefore minimized. From Fig. 7, the corresponding mean temperature over the normally irradiated length is 512° C., but, as shown in Fig. 6, for

temperatures in this region the temperature of the central portion is approximately 8° C. higher than the mean temperature over the normally irradiated length. Thus the effective temperature over the central portion may be estimated, by a combination of the X-ray temperature calibration and the thermocouple measurements, as 520° C., in excellent agreement with the value of 522° C. derived entirely from the measured lattice spacing using a 1-mm. beam. In another experiment, a similar exposure was made with the 1-mm. beam raised above the central line by approximately 1 mm. From the measured gradients, the temperature of the specimen at this height should be approximately 7° C. lower than at the exact centre, again in excellent agreement with the temperature of 516° C. calculated from the lattice spacing. These experiments show that the X-ray method, using beams of small dimensions, may be used to evaluate the temperature gradients in the specimen, and that results are obtained in agreement with thermocouple measurements, with the thermocouple wires sealed to dummy specimens. Owing to the long exposures necessary with small beams, and the difficulty of accurate height adjustment, the thermocouple technique is in general the more convenient.

VII.—QUALITY OF FILMS.

In general, high-quality films were obtained from silver-wire specimens at temperatures up to 550° C., with the lines resolved down to line 11, which occurs at a Bragg angle of approximately 38° with copper radiation. Occasionally the resolution of this line was poor, and it was considered that the resolution of line 11 might be taken as an index of the quality of the temperature control during exposure. Temperature variations which cause the α_1 component for the lowest temperature reached to overlap the α_2 component for the highest temperature reached would totally destroy resolution, which would be expected to be poor if the α_1 component for the lowest temperature fell midway between the α_1 and α_2 components for the highest temperature. Calculation shows that a total temperature change of approximately 100° C. would be necessary to destroy resolution of line 11 entirely, while a variation of approximately $\pm 25^{\circ}$ C. would be needed for the low-temperature α_1 component to fall midway between the high-temperature α_1 and α_2 components. Thus, neither the temperature control ($\pm 0.4^{\circ}$ C. in these experiments), nor temperature variations of the magnitude shown in Fig. 6, can have appreciable influence on the resolution of line 11, which may be taken as an index of the quality of other experimental arrangements, such as eccentricity or asymmetry of the specimen.

VIII.—SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS.

From experience gained in exploratory work with a Unicam high-temperature Debye-Scherrer X-ray camera, it is concluded that no method involving movable thermocouples is entirely satisfactory either for exploring the temperature distribution in the furnace gap or for measuring the temperature of the specimen during an exposure. A reliable method for examining the temperature gradients has been developed, in which fine thermocouple wires are attached in given positions to a dummy specimen. Measurements made in this way, provided that adequate precautions are taken, are in good agreement with X-ray determinations of the mean specimen temperature over the irradiated length. The temperature distributions measured for the camera employed in this work vary from $\pm 2.25^{\circ}$ C. at 200° C. to $\pm 5.5^{\circ}$ C. at 541° C., and suggest that the 7-mm. gap between the upper and lower furnaces is excessive. Among the precautions which should be taken, in both calibration and experimental runs, are :

(i) The positions of the controlling and reference thermocouples should be rigidly standardized.

(ii) Connections between thermocouple wires and compensating leads in situations subject to temperature variations should be eliminated by continuing the actual thermocouple wires back to the cold-junction box.

(iii) The specimen should be exactly symmetrically situated about the central point of the furnace gap.

(iv) The specimen should be thermally insulated from the holder.

(v) The temperatures of the upper and lower furnaces should be capable of easy and rapid adjustment to equality.

(vi) The furnace temperature should be accurately controlled.

A differential-thermocouple device, which should also be rigidly fixed, is described for adjusting furnace temperatures to equality, while a circuit giving overall control of $\pm 0.4^{\circ}$ C., in conjunction with an Ether-Wheelco "Capacitrol" regulator, is recommended. It is advisable to stabilize the mains' voltage to obtain maximum stability over long periods.

It is recommended that, for the assessment of specimen temperature, internal calibration against the lattice spacings of a standard substance be used. Care must be taken, however, since the experiments carried out show clearly that if calibration experiments are carried out using a bright specimen, and experiments are subsequently carried out with specimens of higher emissivity, errors of up to 20° C. may occur in the

assessment of the specimen temperature at 500° C. This error, which has not previously been pointed out, increases as the temperature is raised. It appears to be essential to calibrate the thermocouple using specimens of the same emissivity as those to be used in subsequent experiments. If silica containers are to be used in the latter case, the calibration specimen must also be similarly enclosed. If wire specimens are used, the surfaces should in all cases be in a comparable condition, either all polished, or all equally blackened artificially, as, for instance, with colloidal graphite. In cases where this is impossible, the comparison of mean temperatures as deduced from the gradient measurements and the X-ray measurements reported in this paper, suggests that the measuring thermocouple may be calibrated in terms of the gradient measurements without too great a loss of accuracy, provided that the effective irradiated specimen length is known.

The authors are unaware of any previous detailed examination of the temperature gradients in the furnace gap in this type of equipment. The results obtained suggest that the gradients present are larger than is usually recognized, and that unsuspected errors may arise from this cause.

ACKNOWLEDGEMENTS.

This work forms part of a more general programme, in progress in the Department of Metallurgy, Birmingham University, under the general guidance of Professor D. Hanson. Grateful acknowledgement is made to Imperial Chemical Industries, Ltd., for the loan of the camera, and other assistance.

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1. W. Hume-Rothery and P. W. Reynolds, *Proc. Roy. Soc.*, 1938, [A], 167, 25.

THE TENSILE PROPERTIES OF HEAT-TREATED ALUMINIUM-COPPER AND ALUMINIUM-COPPER-CADMIUM ALLOYS OF COMMERCIAL PURITY.*

By H. K. HARDY,† Ph.D., M.Sc., A.R.S.M., A.I.M., MEMBER.

SYNOPSIS.

Previous work (*J. Inst. Metals*, 1950-51, **78**, 169) showed that additions of cadmium accelerated the artificial ageing and markedly increased the strength properties of cast and heat-treated aluminium-4% copper-0.15% titanium alloys of very high purity. Aluminium-copper-cadmium alloys of normal purity have now been examined in the cast or wrought condition. Alloys with more than 0.1% cadmium were hot short and generally failed to forge. The quantity of cadmium was not critical in the case of cast alloys, and up to 0.5% had no detrimental effect on the ductility of fully heat-treated test-bars at room temperature.

Cadmium additions increased the strength properties of artificially aged aluminium-copper alloys to an important extent and slightly improved the resistance to corrosion by salt spray. Such alloys merit consideration for industrial use. The effect of cadmium was not influenced by the presence of iron, silicon, manganese, zinc, nickel, or 0.05% magnesium.

Cadmium additions did not affect the ageing at 132° C. of wrought aluminium-zinc-magnesium and aluminium-zinc-magnesium-copper alloys.

I.—INTRODUCTION.

RECENT investigation of the effect of small quantities of third elements on the ageing characteristics of the cast and heat-treated aluminium-4% copper-0.15% titanium alloy proved that the presence of cadmium markedly influenced the precipitation process.¹ Cadmium additions, of the order of 0.05-0.1 wt.-%, were found to retard natural ageing but greatly to accelerate artificial ageing at 165° C. In addition, the proof- and maximum-stress values after artificial ageing were substantially increased without making the alloys undesirably brittle.

The original work was confined to cast alloys of very high purity, and the investigation has now been extended to cover the effect of cadmium additions to a wide range of cast or wrought aluminium alloys. The present paper marks a development stage between the discovery of the effects and their possible technical utilization.

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The work described below forms part of a general study of precipitation phenomena in aluminium-copper alloys and had the following objectives:

(1) To determine the effect of cadmium additions on the tensile properties of cast or wrought aluminium-copper alloys of normal purity.

(2) To determine whether the influence of cadmium on aluminium-copper alloys is affected by the presence of other elements such as iron, silicon, manganese, magnesium, zinc, or nickel.

(3) To investigate the effect of small quantities of cadmium on the tensile properties of aluminium-zinc-magnesium and aluminium-zinc-magnesium-copper alloys.

II.—EXPERIMENTAL PROCEDURE.

1. *Preparation of the Alloys.*

The aluminium-copper alloys were melted in a high-frequency furnace, and the aluminium-zinc-magnesium alloys were made in an oil-fired furnace. The melts, which were approximately 12 lb. in weight, were chlorine-degassed through an alumina tube. When the alloys were to be tested in the cast condition, D.T.D. test-bars were cast in baked sand moulds at controlled pouring temperatures. Forging billets were cast by pouring into a cylindrical thin sheet steel container and allowing water in an annular space between this and an outer container to rise at such a rate that directional solidification occurred from the bottom of the ingot.

The forging billets were scalped to $2\frac{1}{4}$ in. dia., and the aluminium-copper alloys were homogenized for 16 hr. at 480°C ., pre-heated for 2 hr. at 460°C ., and forged at this temperature to $\frac{3}{4}$ in. square. The aluminium-zinc-magnesium and aluminium-zinc-magnesium-copper alloys were homogenized, pre-heated, and forged at 400°C .

Alloys with 0.05% cadmium forged satisfactorily but showed slightly more corner cracking than the cadmium-free alloys. Alloys with 0.25% cadmium were hot short and normally failed to forge. A cadmium content of 0.1% represented a reasonable choice of the permissible upper limit under the experimental conditions used. No difference was noted between aluminium-copper-cadmium and aluminium-copper-magnesium-cadmium alloys containing 0.25% cadmium, both of which failed to forge through hot shortness. It had been shown earlier² that 0.3% tin rendered aluminium-copper alloys hot short, but that an aluminium-copper-0.5% magnesium alloy forged satisfactorily when containing this quantity of tin.

2. Analyses.

Melt analyses were made in all cases, and the compositions of any given group of alloys were very close to the mean values. Consequently, only the average values for each set of alloys are given in the tables.

3. Heat-Treatment.

The test-bars were heat-treated in a circulating-air furnace, the details being given in the tables. The aluminium-copper alloys were aged 14 days at room temperature or artificially aged. In order to simplify the heat-treatment schedules, only one artificial-ageing treat-

TABLE I.—*Effect of Cadmium Additions on Tensile Properties of Cast Al-4.5% Cu Alloys with Various Iron and Manganese Contents.*

Averaged results on sand-cast D.T.D. test bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as shown.

Ref. No.	Cadmium Addition, %	Aged 14 days at room temperature			Aged 16 hr. at 165° C.		
		0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %
<i>Low-Iron (Cu 4.5, Fe 0.22, Si 0.1, Ti 0.15%)</i>							
F411 } F471 }	Nil	7.6	17.7	17	14.9	21.9	6
F412	0.05	7.5	16.6	14	19.5	23.3	3
F413	0.1	6.8	16.5	15	23.0	24.6	2
F414	0.25	6.1	15.8	15	24.1	25.4	2½
F416	0.5	6.1	17.0	17½	23.6	26.6	2½
<i>Medium-Iron (Cu 4.5, Fe 0.44, Si 0.2, Ti 0.15%)</i>							
F417 } F472 }	Nil	6.0	12.9	7	9.7	14.6	6
F418	0.05	6.1	13.2	7	20.7	21.0	2
F419	0.1	5.7	13.5	8½	20.2	22.0	2
F420	0.25	5.5	12.5	7	20.7	21.7	2½
F421	0.5	4.9	12.6	7½	20.9	20.8	1½
<i>Medium-Iron-Medium-Manganese (Cu 4.5, Fe 0.3, Mn 0.46, Si 0.1, Ti 0.14%)</i>							
F475	Nil	7.0	15.5	10	15.2	19.5	4
F476	0.075	6.7	15.9	9½	23.4	25.5	2

ment was employed, and 16 hr. at 165° C. was chosen as being suitable for all the aluminium-copper alloys, although not necessarily giving the highest properties.

The aluminium-zinc-magnesium and aluminium-zinc-magnesium-copper alloys were aged at 132° C. after a controlled period of room temperature ageing. Single test-pieces were used for these alloys.

In general, duplicate test-pieces were used for all the aluminium-copper alloys, although occasionally these were tested in triplicate or quadruplicate. In all cases only the averaged results have been given (see Tables I-VIII).

III.—TENSILE-TEST RESULTS.

1. Cast or Wrought Al-4.5% Cu Alloys with Various Iron and Manganese Contents.

The tensile-test results are given in Tables I and II. The tensile properties both of the cast and wrought alloys were reduced by increasing the iron content, but were not significantly affected by the presence

TABLE II.—Effect of Cadmium Additions on Tensile Properties of Wrought Al-4.5% Cu Alloys with Various Iron and Manganese Contents.

Averaged results on 2½-in.-dia. billets hot forged to ¾ in. square, solution heat-treated 2 hr. at 530° C., cold-water quenched, and aged as shown.

Ref. No.	Cadmium Addition, %	Aged 14 days at room temperature			Aged 16 hr. at 165° C.		
		0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %
<i>Low-Iron (Cu 4.5, Fe 0.24, Si 0.1%, Ti nil)</i>							
F455	Nil	6.0	17.1	35	9.4	19.3	22½
F456	0.08	5.8	16.6	32½	21.6	26.7	15
<i>Medium-Iron (Cu 4.5, Fe 0.40, Si 0.2, Ti 0.16%)</i>							
F468	Nil	5.7	16.8	32	6.9	16.8	28
F469	0.08	5.6	16.0	35	20.1	25.3	15
<i>Low-Iron-Medium-Manganese (Cu 4.5, Fe 0.19, Si 0.1, Mn 0.5%, Ti nil)</i>							
F461	Nil	6.5	17.3	32	9.9	19.5	27½
F462	0.08	6.1	17.2	32½	23.1	27.9	16½
<i>Medium-Iron-Low-Manganese (Cu 4.5, Fe 0.41, Si 0.22, Mn 0.25, Ti 0.15%)</i>							
F395	Nil	5.4	15.5	30	7.0	16.6	27
F396	0.08	5.7	16.4	31	15.7	22.8	14
F397	0.25	5.6	16.3	28	18.0	23.9	15

of up to 0.5% manganese. This effect of iron is well known and is probably due to the formation of an insoluble Al-Cu-Fe constituent, thus reducing the copper content of the solid solution.^{3, 4}

Cadmium additions raised the tensile properties after artificial ageing in all cases. The quantity of cadmium required for this purpose was largely independent of the iron and manganese content. It may

be noted that the presence of 0.5% cadmium did not render the cast alloy abnormally brittle after artificial ageing. This confirmed the behaviour in alloys of very high purity¹ and leads to the conclusion that undissolved cadmium is not detrimental, in contrast to the effect of excess tin additions which cause severe embrittlement at room temperature.²

2. Cast Al-4.5% Cu-0.05% Mg Alloys with Various Iron Contents.

Table III sets out tensile-test results. Cadmium additions materially increased the strength properties in the artificially aged condition for both the iron levels investigated.

TABLE III.—*Effect of Cadmium Additions on Tensile Properties of Cast Al-4.5% Cu-0.05% Mg Alloys with Various Iron Contents.*

Averaged results on sand-cast D.T.D. test-bars, solution heat-treated 16 hr. at 530° C., cold-water quenched, and aged as shown.

Ref. No.	Cadmium Addition, %	Aged 14 days at room temperature			Aged 16 hr. at 165° C.		
		0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %
<i>Low-Iron (Cu 4.5, Mg 0.05, Fe 0.24, Si 0.1, Ti 0.14%)</i>							
F473	Nil	10.0	18.5	9½	13.9	19.5	5
F474	0.08	8.5	19.0	17½	24.6	26.5	3
<i>Medium-Iron (Cu 4.5, Mg 0.05, Fe 0.45, Si 0.2, Ti 0.14%)</i>							
F422	Nil	11.5	17.2	6	12.0	17.7	4½
F423	0.08	10.0	17.3	7	22.3	23.7	2

3. Wrought Al-Cu-0.5% Mg Alloys with Various Iron, Silicon, and Manganese Contents.

The tensile-test results are given in Table IV. The addition of 0.5% magnesium greatly increased the strength properties of the cadmium-free aluminium-4.5% copper alloy (cf. Tables II and IV). The properties in the artificially aged condition received a further slight increase from the presence of cadmium (Table IV). This result has been confirmed on the complex aluminium-4.2% copper-0.5% magnesium alloy (D.T.D. 364B composition). The addition of 0.3% tin to this alloy had been found previously² to have no significant effect.

Cadmium additions may thus exercise a slight beneficial influence on the properties of aluminium-copper-magnesium alloys and this

is unaffected by small quantities of iron, silicon, and manganese present simultaneously.

TABLE IV.—Effect of Cadmium on Tensile Properties of Wrought Al-Cu-0.5% Mg Alloys with Various Iron, Silicon, and Manganese Contents.

Averaged results on 2½-in.-dia. billets hot forged to ¾ in. square, solution heat-treated 2 hr. at 510° C., cold-water quenched, and aged as shown.

Ref. No.	Cadmium Addition, %	Aged 14 days at room temperature			Aged 16 hr. at 165° C.		
		0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elongation, %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elongation, %
<i>Low-Iron (Cu 4.5, Mg 0.45, Fe 0.13, Si 0.1%, Ti nil)</i>							
F458	Nil	15.3	25.4	33	20.5	26.6	16½
F459	0.08	15.2	25.7	34	22.6	28.2	13
<i>Medium-Iron (Cu 4.5, Mg 0.56, Fe 0.41, Si 0.16, Ti 0.16%)</i>							
F398	Nil	14.8	25.8	30	18.5	25.5	18
F399	0.05	13.5	24.6	29	19.5	26.0	15
F400	0.08	13.9	25.3	29	20.7	27.2	14
F401	0.1	—	—	—	21.1	28.1	13
<i>D.T.D. 364B Composition (Cu 4.2, Mg 0.5, Fe 0.9, Si 0.6, Mn 0.6, Ti 0.15%)</i>							
F404	Nil	14.9	27.9	21	20.8	26.8	12
F405	0.08	14.5	27.1	24	25.1	29.8	12

TABLE V.—Effect of Cadmium Additions on Tensile Properties of Wrought Al-3% Cu-5% Si Alloys with Various Iron Contents.

Averaged results on 2½-in.-dia. billets hot forged to ¾ in. square, solution heat-treated 2 hr. at 510° C., cold-water quenched, and aged as shown.

Ref. No.	Cadmium Addition, %	Aged 14 days at room temperature			Aged 16 hr. at 165° C.		
		0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %
<i>Low-Iron (Cu 3.0, Si 4.9, Fe 0.25%, Ti nil)</i>							
F452	Nil	5.5	17.3	27½	7.3	18.2	22
F453	0.08	5.6	17.3	28½	15.3	23.0	15
<i>Medium-Iron (Cu 3.0, Si 4.8, Fe 0.42, Ti 0.14%)</i>							
F392	Nil	5.4	17.1	30	6.7	17.6	23
F393	0.08	5.6	17.6	26	16.7	20.1	14
F394	0.25	5.5	17.9	29	12.2	20.6	13

4. Wrought Al-3% Cu-5% Si Alloys with Various Iron Contents.

The increased properties of the artificially aged material containing cadmium were unaffected by the addition of 5.0% silicon. Tensile-test results are given in Table V.

5. Cast Al-3% Cu Alloys with Various Silicon, Zinc, or Nickel Contents.

Table VI summarizes the tensile-test results. Additions of cadmium increased the strength properties of all the alloys after artificial ageing.

TABLE VI.—Effect of Cadmium Additions on Tensile Properties of Cast Al-3% Cu Alloys with Various Silicon, Zinc, or Nickel Contents.

Averaged results on sand-cast D.T.D. test-bars, solution heat-treated (Ni-containing alloys 16 hr. at 530° C.; other alloys 16 hr. at 510° C.), cold-water quenched, and aged as shown.

Ref. No.	Cadmium Addition, %	Aged 14 days at room temperature			Aged 16 hr. at 165° C.		
		0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elonga- tion, %
<i>Cu 3, Si 3.3, Fe 0.35, Ti 0.15%</i>							
F480	Nil	5.8	11.7	4	6.2	12.3	3½
F481	0.08	5.4	12.8	5½	14.3	16.8	1
F482	0.3	5.3	12.7	6	15.5	18.0	2
<i>Cu 3, Si 12, Fe 0.3, Ti 0.15% (Modified)</i>							
F535	Nil	6.0	9.3	2½	9.3	12.0	2
F496	0.08	6.8	11.7	1½	13.9 *	14.3	2
F497	0.3	6.7	10.2	2	14.5 *	15.4	1½
<i>Cu 3, Zn 5, Fe 0.3, Si 0.2, Ti 0.15%</i>							
F565	Nil	4.8	11.8	11½	5.0	12.4	10½
F566	0.08	4.9	12.3	11	13.3	16.2	4
<i>Cu 3, Ni 1, Fe 0.4, Si 0.16, Ti 0.15%</i>							
F492	Nil	5.4	13.6	11½	4.9	12.0	4½
F493	0.08	5.0	13.0	12	13.6	17.3	6½
F494	0.3	5.2	13.2	12	15.1	18.8	4

* 0.05% proof stress.

Good combinations of strength and ductility were obtained in cadmium-containing alloys with 3% silicon or 1% nickel, but the alloy with 12% silicon had an unduly high proof stress : maximum stress ratio in the artificially aged condition.

IV.—CORROSION TESTS ON WROUGHT ALLOYS.

Tensile test-pieces of the wrought aluminium-4.5% copper alloys of Table II, with and without additions of cadmium, were subjected in

the artificially aged condition to corrosion by spraying once each day for 3 months with 3% sodium chloride solution. The test results are given in Table VII, together with the values for the uncorroded bars.

TABLE VII.—*Effect of Cadmium Additions on Corrosion-Resistance of Wrought Al-4.5% Cu Alloys with Various Iron and Manganese Contents.*

Averaged tensile-test results on 2½-in.-dia. billets hot forged to ¾ in. square, solution heat-treated 2 hr. at 530° C., cold-water quenched, and aged 16 hr. at 165° C. Duplicate test-pieces, 0.423 in. in dia., sprayed once each weekday for 3 months with 3% sodium chloride solution.

Ref. No.	Cadmium Addition, %	Uncorroded		Corroded		Reduction in Max. Stress, tons/in. ²	Equivalent Mean Reduction in Dia., in.
		Max. Stress, tons/in. ²	Elongation, %	Max. Stress, tons/in. ²	Elongation, %		
Low-Iron (Cu 4.5, Fe 0.24, Si 0.1%, Ti nil)							
F455	Nil	17.8	26	13.5	13	4.3	0.055
F456	0.08	26.0	15	24.5	12	1.5	0.013
Medium-Iron (Cu 4.5, Fe 0.40, Si 0.2, Ti 0.16%)							
F468	Nil	16.5	29	13.8	18	2.7	0.036
F469	0.08	24.6	16	23.4	11	1.2	0.010
Low-Iron-Medium-Manganese (Cu 4.5, Fe 0.19, Si 0.1, Mn 0.5%, Ti nil)							
F461	Nil	18.4	24	17.1	19	1.3	0.015
F462	0.08	27.3	16½	25.9	12½	1.4	0.011

It will be seen that the reduction in maximum strength and elongation has generally been less for the alloys with additions of cadmium than for cadmium-free alloys. Microscopic examination showed intracrystalline pitting in the alloys containing cadmium and intercrystalline corrosion in the cadmium-free alloys.

It may safely be concluded that cadmium additions do not militate against the corrosion-resistance of wrought alloys and may exert a beneficial effect. This probably results from the fact that the resistance to corrosion passes through a minimum after a short time of artificial ageing, and a given ageing treatment causes proportionally greater precipitation in alloys containing cadmium than in the cadmium-free alloys.

V.—EFFECT OF CADMIUM ON AL-ZN-MG ALLOYS.

Table VIII gives the tensile-test results after various periods of ageing at 132° C. for wrought aluminium-zinc-magnesium alloys with and without 1.5% copper. It will be seen that the additions of cadmium

had no significant influence on the rate of ageing or the level of properties for either the copper-free or the copper-containing alloys. The

TABLE VIII.—*Effect of Cadmium Additions on Ageing Properties of Wrought Al-Zn-Mg * and Al-Zn-Mg-Cu Alloys.*

Tensile-test results on $2\frac{1}{4}$ -in.-dia. billets hot forged to $\frac{3}{4}$ in. square, solution heat-treated $1\frac{1}{2}$ hr. at 460° C., cold-water quenched, held 8 days at room temperature and aged as shown.

Ageing Time at 132° C.	0.1% Proof Stress, tons/in. ²	Max Stress, tons/in. ²	Elongation, %	0.1% Proof Stress, tons/in. ²	Max Stress, tons/in. ²	Elongation, %
<i>Copper nil—Cadmium nil</i>				<i>Copper nil—Cadmium 0.05%</i>		
4 hrs.	28.3	31.7	16	27.6	31.8	16
9 hrs.	28.9	31.9	16	28.0	31.6	17
16 hrs.	28.1	31.1	13	26.5	30.6	12
1 day	30.1	32.2	17	28.0	31.9	15
2 days	27.4	31.4	15	26.4	30.1	17
<i>Copper 1.5%—Cadmium nil</i>				<i>Copper 1.5%—Cadmium 0.05%</i>		
4 hrs.	30.0	35.2	16	29.0	35.2	17
8 hrs.	30.5	35.7	15	29.4	33.9	15
16 hrs.	31.0	35.4	10	29.4	34.8	13
1 day	31.1	35.5	16	30.6	34.6	15
2 days	31.1	35.4	13	30.6	34.8	15

* Composition : Zn 5.8, Mg 2.5, Fe 0.32, Si 0.14, Mn 0.2, Cr 0.14, Ti 0.15%; Cu and Cd as shown; Al remainder.

presence of 1.5% copper increased the maximum-stress values to a slightly greater extent than the proof-stress values.

VI.—DISCUSSION OF RESULTS.

Cadmium additions greatly increased the strength properties in the artificially aged condition for substantially all the cast or wrought aluminium-copper alloys investigated. This behaviour, and the quantity of cadmium required, was unaffected by the simultaneous presence of iron, silicon, and manganese, and by separate additions of silicon, nickel, zinc, or small quantities of magnesium. A slight improvement was also produced in alloys containing 0.5% magnesium.

The retardation of natural ageing noted previously with high-purity material¹ proved to be less marked in these alloys. Nevertheless, aluminium-copper and aluminium-copper-cadmium alloys age naturally much more slowly than aluminium-copper-magnesium alloys of the Duralumin type. The slow ageing of such alloys would allow them to be cold formed at a much later date after solution heat-treatment than is the case for aluminium-copper-magnesium alloys, subsequent artificial ageing providing properties approaching those shown by

alloys of the Duralumin type. A slight reduction in tensile properties would be more than offset for many applications by the greater ease of hot working of aluminium-copper alloys compared with Duralumin-type alloys.

The response of the cast aluminium-4.5% copper alloy to heat-treatment is well known to be erratic. It has been suggested earlier² that this results from the accidental occurrence of small quantities of tin. Tin additions are not easily controlled, because the quantity added has to be balanced against the small amounts of magnesium frequently present in the alloy.¹ Cadmium additions may be used to obtain a controlled response to heat-treatment of aluminium-copper alloys. The quantity required is much less critical than in the case of tin, because the effect of cadmium is not influenced by the presence of small amounts of magnesium, and excess cadmium does not render the cast and heat-treated alloys unduly brittle.

In addition, it should be possible to select a medium-strength alloy based on aluminium-copper-silicon-cadmium which would possess good casting characteristics. Similarly, a wrought medium-strength aluminium-copper-silicon-cadmium alloy might prove suitable for easy welding.

It is not intended to discuss the mechanism of the effect of cadmium additions on the ageing processes of aluminium-copper alloys, as present views have been described very recently.¹ Cadmium additions had no effect on aluminium-zinc-magnesium and aluminium-zinc-magnesium-1.5% copper alloys. This is not surprising, if the suggestion that cadmium atoms become surrounded by copper atoms during solution heat-treatment is correct,¹ and if the precipitation process in these alloys involves more than one type of solute atom.

The increase in strength properties and other features mentioned above are thought to be sufficiently important to make aluminium-copper-cadmium alloys worth consideration for industrial use.⁵

ACKNOWLEDGEMENTS.

The author's thanks are due to his colleagues at the Fulmer Research Institute who contributed to the experimental work.

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4. H. Y. Hunsicker, "Age-Hardening of Metals," p. 56. Cleveland, O.: 1940. (American Society for Metals).
5. Patents applied for.

REPORT OF COUNCIL

for the Year Ended 31 December 1950.

DURING the year 1950, the Institute has made steady progress, and its various activities have been well maintained.

The arrangements for the Annual General Meeting in London departed from previous practice in that, in place of a dinner-dance, a luncheon was held, at which the Institute of Metals (Platinum) Medal was presented to the distinguished French metallurgist Professor Albert Portevin. The occasion was honoured by the presence of His Excellency the French Ambassador, M. Massigli. In addition to the scientific meetings, a *Conversazione* was also held at the Institute's headquarters, in connection with which there was an interesting display of scientific exhibits. Both of these social occasions were very well attended by Members and their friends. During the course of the meetings there took place a successful symposium on "Metallurgical Aspects of the Hot-Working of Non-Ferrous Metals and Alloys". The series of symposia on technological subjects that have been arranged in recent years, of which this was one, have been widely appreciated, and other such meetings on technological subjects will be arranged in future. The recently formed Metallurgical Engineering Committee is getting into its stride, and will become particularly active in this connection.

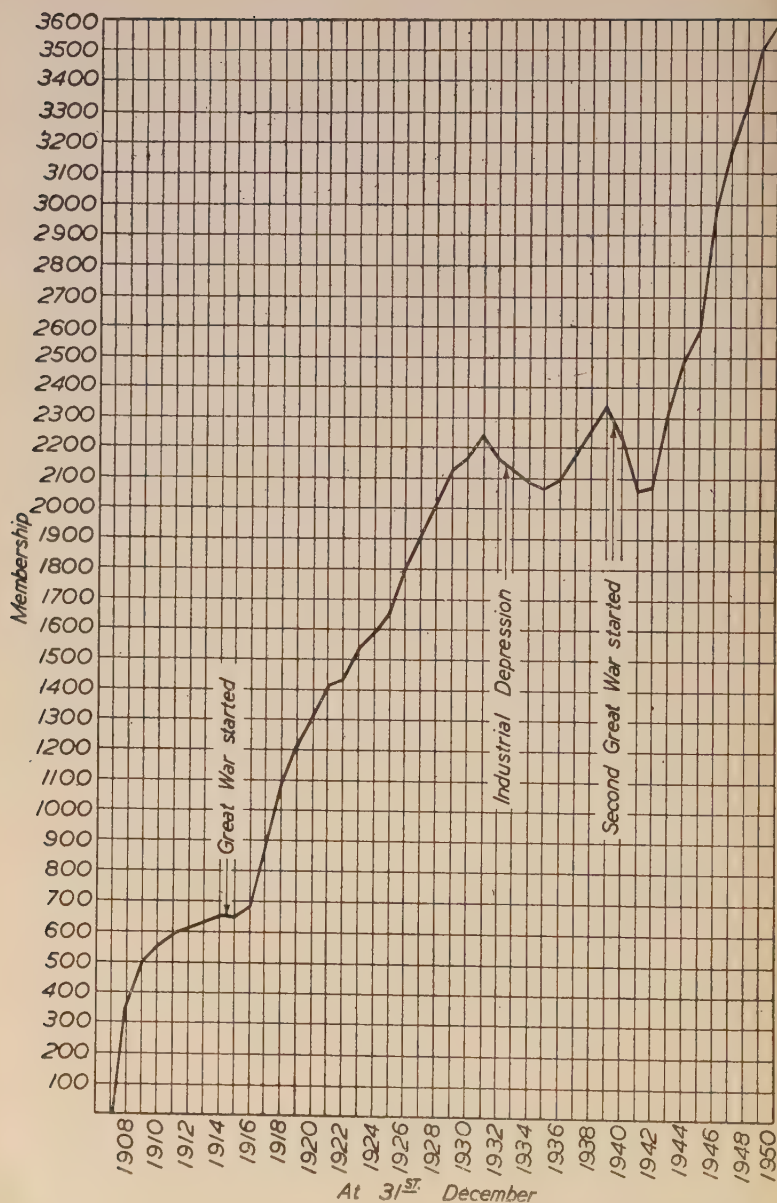
The Autumn Meeting was held at Bournemouth. All the functions were evidently enjoyed, and the scientific meetings were well attended. The Twenty-First Autumn Lecture was delivered by Mr. Earle E. Schumacher of the Bell Telephone Laboratories, Inc., U.S.A. The lecture was a particularly valuable contribution and attracted a large audience.

Apart from these general meetings, the Local Sections of the Institute and the Associated Societies will, during the 1950-51 winter session, hold no fewer than sixty-four meetings in various industrial centres.

Consideration is being given to the type of meeting, particularly General Meeting, which will be most useful and agreeable to the widest possible range of members in the changing conditions of our times, and a Committee has been set up to consider this problem. Meanwhile, the Council has accepted an invitation from the *Associazione Italiana di Metallurgia* to hold the 1951 Autumn Meeting in Italy, synchronously with the meeting of our Italian friends, and it is hoped that many members will join in this opportunity of extending their foreign friendships.

During the year it was decided to create a new category of Junior Members, between Student Members and Ordinary Members, so that those who join in their student days may make a more gradual progress to full membership. The opportunity was taken to revise the Articles of Association of the Institute in various ways, and an Extraordinary General Meeting was held in June, at which these changes were approved by the Members.

The attention of the Council has been applied closely to the problem of the Institute's finances. Owing to the greatly increased cost in every department of its activities, and also to the expansion of those activities, the annual expenditure, in spite of the increase in the rate of subscription which was made in 1947, had outstripped the income of the Institute by something like £2000 per annum on the ordinary Income and Expenditure Account, and, in addition to this, certain definite further increases in expenditure are known to be



Curve of Active Membership of the Institute at 31 December 1908-1950.

pending. In these circumstances, the Council decided that an appeal should be made to firms in the metallurgical and allied industries, whose progress is dependent on the advancement of metallurgical science, for regular yearly support under covenant, in order that the finances of the Institute might be placed on a really stable basis. It is confidently believed that this support will be forthcoming, and that the anxiety with which the Council has been viewing the situation will be relieved.

FELLOW.

During the year, Mr. William Henry Henman was elected a Fellow, in recognition of his eminent services to the Institute.

MEMBERSHIP.

A steady increase in membership has been maintained, as will be seen from the following table. It is considered, however, that the membership is capable of considerable expansion—particularly on the industrial side, and it is hoped that during 1951 members will, individually and collectively, take really active steps in all countries to bring the advantages of membership to the notice of their friends. Membership is international, and the Institute endeavours to serve science and industry without regard to nationality, etc.

At 31 December	1943	1944	1945	1946	1947	1948	1949	1950
Honorary Members .	6	6	6	6	9	9	11	11
Fellows	7	7	6	6	7	6	9	10
Ordinary Members .	2018	2153	2213	2414	2491	2546	2685	2815
Junior Members	291
Associate Members .	15	15	12	25	17	19	18	...
Student Members .	267	305	361	529	655	746	783	452
Active List . . .	2313	2486	2598	2980	3179	3326	3506	3579
Suspense List . .	195	200	179	53	36	55	67	97
Total	2508	2686	2777	3038	3215	3381	3573	3676

A new 4to pamphlet, entitled "The Institute of Metals: Particulars of its Objects, Work, and Membership", has been printed, and copies can be obtained, on application, by all who require them for membership development purposes.

As is mentioned earlier in this Report, during the past year the Institute's Articles of Association were revised to make provision for a class of "Junior Members"; at the same time it was decided to allow the "Associate Member" class to pass into abeyance, because of the small numbers of those who, over a period of years, have taken advantage of the privileges offered.

OBITUARY.

The Council deeply regrets to record the deaths of Lieut.-Colonel Sir John Greenly, Past-President, Fellow, and Institute of Metals (Platinum) Medallist, and Mr. Roosevelt Griffiths, a former Vice-President of the Institute and former Chairman of the Swansea (now South Wales) Local Section.

It also much regrets to record the deaths of the following members, which were notified during the year: Mr. M. Alexander; Mr. F. A. Allen; Mr. D.

Basch; Mr. G. B. Brook; Mr. J. Curran; Mr. R. B. Deeley; Dr. H. A. Dickie; Capt. J. H. Farmer; Mr. P. Friedmann; Dr. H. W. Gillett; Mr. M. M. Goldsmith; Mr. G. E. Heyl; Mr. F. H. Hurren (an Original Member); Mr. R. S. Kirkwood; Mr. A. Glynne Lobley; Mr. R. J. McLeod; Dr. F. W. Meyer; Mr. A. P. Newall; Mr. C. S. Scott; Mr. J. G. Simpson; Mr. A. D. Storke; and Mr. K. W. Winsor.

OFFICERS OF THE INSTITUTE.

The following members were declared elected to fill vacancies as honorary officers of the Institute with effect from the 1950 Annual General Meeting:

President :

H. S. TASKER, B.A.

Vice-Presidents :

Professor H. O'NEILL, D.Sc., M.Met.

Professor F. C. THOMPSON, D.Met., M.Sc.

Ordinary Members of Council :

G. L. BAILEY, M.Sc.

HARRY DAVIES.

E. H. JONES.

L. B. PFEIL, O.B.E., D.Sc., A.R.S.M.

Professor G. V. RAYNOR, D.Sc., D.Phil., M.A.

In accordance with Article 42, the Council elected Professor A. J. MURPHY, M.Sc., as Senior Vice-President for the year 1950-51.

HONORARY CORRESPONDING MEMBERS TO THE COUNCIL.

M. Jean Matter was appointed an additional Honorary Corresponding Member to the Council for France.

The Council desires to express to all Honorary Corresponding Members its appreciation for their help and advice during the past year. The list of Honorary Corresponding Members to the Council now is as follows: *Argentina*: H. N. Bassett; *Australia*: Professor H. K. Worner, D.Sc.; *Belgium*: H. P. A. Féron; *Canada*: Professor B. Chalmers, Ph.D., D.Sc., and Professor G. Letendre, B.A., Ph.D.; *France*: Professor P. A. J. Chevenard and Jean Matter; *India*: N. P. Gandhi, M.A., B.Sc., A.R.S.M., D.I.C.; *Italy*: Leno Matteoli, Dott.Chim.; *Netherlands*: M. Hamburger; *South Africa*: G. H. Stanley, D.Sc., A.R.S.M., and Professor L. Taverner, A.R.S.M., D.I.C.; *Spain*: Professor J. Orland, M.Sc., M.A., Ph.D., D.D.; *Sweden*: Professor Carl A. F. Benedicks, Fil.Dr., Dr.Ing. e.h., Dr.Techn.h.c.; and Professor Axel Hultgren; *Switzerland*: Professor A. von Zeerleder, Dr.Ing.; *United States of America*: Professor R. F. Mehl, Ph.D., Hon.Eng.D., Hon.Sc.D., Professor C. S. Smith, Sc.D., and Dr. R. A. Wilkins.

INSTITUTE OF METALS MEDAL.

The Institute of Metals (Platinum) Medal for 1950 was awarded to Professor Albert Portevin, Dr.h.c., Honorary Member, in recognition of his very distinguished services to the science of non-ferrous metallurgy.

W. H. A. ROBERTSON MEDAL.

The first award of the W. H. A. Robertson Medal was made jointly to Mr. W. J. Thomas and Mr. W. A. Fowler for their paper on "Some Technical

Problems Influencing Production Economy in the Rolling of Aluminium" (*Journal*, 1948-49, vol. 75, pp. 921-948).

CAPPER PASS AWARDS.

During the year Capper Pass Awards of £50 each were made: (a) jointly to M. Jean Matter and M. Marcel Lamourdedieu for their paper on "The New Factory of the Société Centrale des Alliages Légers at Issoire (Puy-de-Dôme) for the Working of Light Alloys" (*Journal*, 1948-49, vol. 75, pp. 899-920), and (b) to Dr. E. Scheuer for his paper on "Modern Billet Casting, with Special Reference to the Solidification Process" (*Journal*, 1949-50, vol. 76, pp. 103-120).

WALTER ROSENHAIN MEDAL.

The Council has most gratefully accepted an offer by the Directors of Imperial Chemical Industries, Ltd., to place at their disposal a sum of money to found a Walter Rosenhain Medal.

The medal, which has been designed by Mr. Carter Preston, and is intended to be presented for the first time in 1951, will be awarded annually by the Council in recognition of outstanding contributions in the field of physical metallurgy, made by persons under the age of 45 years, irrespective of nationality, sex, or membership of the Institute.

PUBLICATIONS.

The number of papers and addresses published in the *Journal* in 1950 was 61, an increase of 6 over 1949.

The abstracting of the literature has been brought much more up to date, and the indexing of the annual volumes is considerably more advanced than it was last year. It is expected that the 1949-50 index will be available for distribution early in 1951. Because of staff changes, progress with the decennial index to *Metallurgical Abstracts*, vols. 1-10 (1934-43), was not so well maintained, however, and—though half of the book has already been printed—the volume cannot now be ready before the end of 1951.

After full consideration, and for various reasons which have caused other societies to take the same action, the Council has resolved that the format of the *Journal* shall be changed from octavo to quarto with effect from the issue for September 1951.

In the *Monograph and Report Series* there was published: No. 6: "Symposium on Metallurgical Aspects of Non-Ferrous Metal Melting and Casting of Ingots for Working"; No. 7: "The Solidification of Castings: A Review of the Literature", by R. W. Ruddle; and No. 8: "Metallurgical Applications of the Electron Microscope". In addition No. 9: "Metallurgical Aspects of the Hot-Working of Non-Ferrous Metals and Alloys" is in the press, and two other MSS. have been accepted for publication. These new books will be: No. 10: "Non-Destructive Testing of Metals", by Dr. R. F. Hanstock, F.Inst.P., and No. 11: "Thermodynamics of Alloys", by Mr. John Lumsden, B.Sc., A.R.I.C. Authority has been given for the publication of a German translation of Monograph No. 4: "An Introduction to the Electron Theory of Metals", by Professor G. V. Raynor.

GENERAL MEETINGS.

The Forty-Second Annual General Meeting was held in London from Wednesday to Friday, 29-31 March 1950, when Mr. H. S. Tasker, B.A., was inducted into the Presidential Chair. One day of the meeting was devoted to

an all-day symposium on "Metallurgical Aspects of the Hot-Working of Non-Ferrous Metals and Alloys". The first session of the meeting and a luncheon on the first day were held at the Café Royal, Regent Street, London, W.1, and members appeared to welcome this departure from practice, which provided better facilities than are normally available for social contacts.

On 10 May 1950, before a large audience at the Royal Institution, Albe-marle Street, London, W.1, Dr. H. Roxbee Cox, Chief Scientist, Ministry of Fuel and Power, delivered the Fortieth May Lecture on "Industrial Gas Turbines".

The Forty-Second Annual Autumn Meeting was held in Bournemouth from Monday to Friday, 18-22 September 1950. At that meeting, the Twenty-First Autumn Lecture was delivered by Mr. Earle E. Schumacher, Chief Metallurgist, Bell Telephone Laboratories, Inc., Murray Hill, N.J., U.S.A., on "Communications Metallurgy".

STUDENTS' TOUR.

In the Easter Vacation, from 17 to 21 April 1950, an educational tour to works and laboratories in the Sheffield area was organized for Student Members of the Institute. 27 Student Members took part, and 14 works and laboratories were visited. Though the attendance was considerably smaller than in the previous year, there seems to be no doubt that these tours meet a real need, and it is intended to continue them annually. The 1951 tour will be held, in the Easter Vacation, in the Swansea area.

The Council records its gratitude to the Directors of the works and laboratories visited, and to the local advisory Committee, for their co-operation in making this tour a success.

LOCAL SECTIONS AND ASSOCIATED SOCIETIES.

The five Local Sections (Birmingham, London, Scottish, Sheffield, and South Wales) have been active and arranged good programmes of meetings for the winter session. Members of the Institute continued to enjoy the privilege of free membership of the Leeds Metallurgical Society and the Manchester Metallurgical Society, and during the year an agreement was reached with the Liverpool Metallurgical Society for members to be granted similar facilities.

The President and Secretary again paid official visits to most of the Local Sections and Associated Societies, and have valued these opportunities to discuss problems of interest to local members.

SPECIAL COMMITTEES.

The Metal Physics Committee has had four meetings during the year, and is organizing a symposium—to be held in the autumn or winter of 1952—on "Properties of Metallic Surfaces". Fourteen papers have already been invited.

The Metallurgical Engineering Committee met four times and is organizing a symposium, to be held in March 1952, on "Equipment for the Thermal Treatment of Non-Ferrous Metals and Alloys". It has also received authority to invite certain papers on problems relating to metallurgical engineering and to arrange local informal meetings to discuss questions relating to metal-working processes.

Ad hoc Committees have also met to discuss proposals relating to the abstracting of metallurgical literature and the publication of reviews of progress in metallurgy.

INTERNATIONAL COLLABORATION BY NATIONAL METALLURGICAL SOCIETIES.

As a result of suggestions made by Dr. Richard Seligman, in a lecture to the Société Française de Métallurgie, for the formation of an "International Metallurgical Association", discussions have taken place on this subject between representatives of the Iron and Steel Institute, the Institution of Mining and Metallurgy, and the Institute of Metals, and also—in Paris—between representatives of those societies and of the Société Française de Métallurgie and the Associazione Italiana di Metallurgia.

So far, no definite proposals have been made as a result of these discussions, but a further meeting is to be held in Paris early in 1951, to which all European national metallurgical societies will be invited to send representatives. It is hoped that, as a result of this meeting, practicable suggestions may be agreed for closer collaboration between the European societies.

STAFF.

The continually increasing activities of the Institute, and the expansion of the *Journal* and *Metallurgical Abstracts*, have made heavy demands on the staff, and the Council desires to place on record its appreciation of the work accomplished.

JOINT ACTIVITIES.

JOINT LIBRARY AND INFORMATION DEPARTMENT.

Every endeavour has been made to maintain and increase the usefulness of the Joint Library for the benefit of members. The expanding use made of the Library is shown by the large yearly increase in the number of publications borrowed since the libraries of the Institute of Metals and the Iron and Steel Institute were amalgamated. In 1939, the first complete year of the Joint Library, 4151 publications were sent out on loan, in 1946 the number was 7514, and in 1950, 11,060 publications were borrowed. During the year under review the Library has been enriched by the addition of 362 text-books, and, on behalf of the Members, the Library Committee extends its thanks to those authors and publishers who have made presentations to the Library during the past year.

Members are reminded that the use of the Lending Library is a valuable privilege of membership. Books and periodicals are sent post free to members resident in Great Britain. In addition to the books filed in the Joint Library, members may borrow—through the Librarian, Mr. R. Elsdon—publications from the Science Library and the National Central Library. Assistance is also given to all members, in Great Britain and overseas, to obtain photostat copies of articles, which can be supplied under certain conditions. A total of 95 photostat copies and 140 microfilms was supplied to members during the past year.

The work of the Information Department is an important part of the service. The Department is prepared to answer scientific and technical enquiries from members, but it is not its function to give the type of advice which comes within the field of the metallurgical consultant.

JOINT COMMITTEE ON METALLURGICAL EDUCATION.

During the year the Sub-Committee on University Courses completed its investigations and issued a printed document entitled "Recommendations on University Full-Time Degree Courses in Metallurgy."

It is intended that the Sub-Committee on Technical College Courses shall

now begin its investigation into Metallurgical Education at Technical Colleges.

JOINT COMMITTEE ON NATIONAL CERTIFICATES IN METALLURGY.

Good progress continues to be made in the scheme for National Certificates in Metallurgy. During the year approved schemes for senior courses leading to an Ordinary National Certificate in Metallurgy were in operation at 24 Technical Colleges (as compared with 22 during the previous year), and schemes for advanced courses leading to a Higher National Certificate at 12 Colleges (as compared with 11 during the previous year).

SIR GEORGE BEILBY MEMORIAL FUND.

During the year, the assessors made awards (for 1949) each of 100 guineas to Mr. F. R. N. Nabarro, in recognition of his application of mathematical methods to the elucidation of the mechanical properties of metals; to Dr. C. E. Ransley, in recognition of his experimental contributions to the knowledge of the behaviour of gases in metals; and to Dr. K. W. Sykes, in recognition of his experimental contributions to the study of the combustion of carbon and its oxidation by steam.

MOND NICKEL FELLOWSHIPS AWARDS.

It is reported that awards were made as follows for 1950 :

Mr. D. Alexander (University of Otago) to study industrial technique and the application of research to metallurgical control in Great Britain, with special reference to tinning, plating, enamelling, and other surface-finishing processes.

Mr. F. R. H. Allon (Southampton). Programme not yet decided.

Mr. K. W. J. Bowen (Cambridge University) to study factors affecting the selection of materials for the construction of chemical and petroleum plant in the U.S.A. and Canada, with particular reference to the influence of research in this field.

Mr. M. G. Gemmill (Sheffield) to study in Britain and the U.S.A. the manufacture, testing, and application of steels for high-temperature service.

Mr. W. B. Hall (Northern Rhodesia) to study American and Canadian plant practice in the hydro-metallurgy and electro-winning of base metals, with special reference to copper and its associate metals, and to make a general study of mechanization and plant management in ore dressing and leaching plants.

APPENDIX.

COMMITTEES.

The main Committees of the Institute which have served during the year were constituted as follows at 31 December 1950 :

Finance and General Purposes Committee.

Major C. J. P. Ball (*Chairman*).
 Mr. E. A. Bolton.
 Mr. C. H. Davy.
 Dr. S. F. Dorey.
 Sir William Griffiths.
 Colonel Sir Paul Gueterbock.
 Mr. H. W. G. Hignett.
 Mr. D. P. C. Neave.
 Sir Arthur Smout.

Ex-officio :

Mr. H. S. Tasker (*President*).
 Professor A. J. Murphy (*Senior Vice-President*).
 Mr. W. A. C. Newman (*Honorary Treasurer*).
 Professor H. O'Neill (*Chairman, Publication Committee*).

Local Sections Committee.

Mr. H. W. G. Hignett (*Chairman*).
 Dr. W. O. Alexander.
 Dr. J. C. Chaston.
 Mr. W. J. G. Cosgrave.
 Dr. J. E. Garside.
 Mr. E. H. Jones.
 Professor A. Preece.

Representatives of Local Sections :

Mr. Bernard Thomas (*Chairman, Birmingham Local Section*).
 Mr. E. H. Bucknall (*Hon. Secretary, Birmingham Local Section*).
 Mr. E. A. G. Liddiard (*Chairman, London Local Section*).
 Dr. E. C. Rhodes (*Hon. Secretary, London Local Section*).
 Mr. H. R. Beauchamp (*Chairman, Scottish Local Section*).
 Mr. Matthew Hay (*Hon. Secretary, Scottish Local Section*).
 Mr. H. G. Dale (*Chairman, Sheffield Local Section*).
 Dr. W. R. Maddocks (*Hon. Secretary, Sheffield Local Section*).
 Mr. E. A. Hontoir (*Chairman, South Wales Local Section*).
 Mr. K. M. Spring (*Hon. Secretary, South Wales Local Section*).

Ex-officio :

Mr. H. S. Tasker (*President*).
 Professor A. J. Murphy (*Senior Vice-President*).
 Mr. W. A. C. Newman (*Honorary Treasurer*).

Medal Committee.

President (*Chairman*).
 Senior Vice-President.

and

Not more than four medallists who are, or have been, Members of Council (selected by the President).

Metal Physics Committee.

Professor A. G. Quarrell (*Chairman*).
 Dr. Maurice Cook.
 Dr. R. F. Hanstock.
 Mr. H. W. G. Hignett.
 Dr. W. Hume-Rothery.
 Mr. Ronald King.
 Mr. D. McLean.
 Mr. F. R. N. Nabarro.
 Mr. D. A. Oliver (*representing the Iron and Steel Institute and the British Iron and Steel Research Association*).
 Professor G. V. Raynor.
 Dr. T. Ll. Richards.
 Mr. L. Rotherham.
 Dr. C. J. Smithells.

Ex-officio :

Mr. H. S. Tasker (*President*).
 Professor H. O'Neill (*Chairman, Publication Committee*).

Metallurgical Engineering Committee.

Mr. D. F. Campbell (*Chairman*).
 Major C. J. P. Ball.
 Mr. W. H. Bowman.
 Mr. C. E. Davies.
 Mr. H. J. Miller.
 Mr. D. P. C. Neave.
 Mr. C. G. Robinson.
 Dr. A. R. E. Singer.
 Mr. Christopher Smith.
 Sir Arthur Smout.
 Dr. N. Swindells.
 Mr. W. J. Thomas.
 Mr. B. N. H. Thornely.

Ex-officio :

Mr. H. S. Tasker (*President*).
 Professor H. O'Neill (*Chairman, Publication Committee*).

Nominations Committee.

President (*Chairman*).
 Colonel Sir Paul Gueterbock.
 Sir Arthur Smout.
 Senior Vice-President.

Publication Committee.

Professor H. O'Neill (*Chairman*).
 Mr. G. L. Bailey.
 Dr. Maurice Cook.
 Dr. F. A. Fox.
 Mr. E. R. Gadd.
 Mr. H. W. G. Hignett (*representing Local Sections Committee*).

Mr. F. Hudson.
 Dr. Ivor Jenkins.
 Mr. E. H. Jones.
 Mr. E. A. G. Liddiard.
 Mr. A. Makower.
 Mr. H. W. L. Phillips.
 Mr. A. R. Powell.
 Professor G. V. Raynor.
 Dr. I. G. Slater.
 Professor F. C. Thompson.

Ex-officio :

Mr. H. S. Tasker (*President*).
 Major C. J. P. Ball (*Chairman, Finance and General Purposes Committee*).
 Mr. W. A. C. Newman (*Honorary Treasurer*).
 Professor A. G. Quarrell (*Chairman, Metal Physics Committee*).
 Mr. D. F. Campbell (*Chairman, Metallurgical Engineering Committee*).

REPORT OF THE HONORARY TREASURER

for the Financial Year Ended 30 June 1950.

The year under review has again been one of enhanced activity in the Institute. The full figures for the period are set out in detail in the accompanying statements, and attention is now drawn to some of the salient features.

As compared with 1948-49, the net income from subscriptions increased by £547 and from the sale of publications and advertisement space together by £681. This latter figure results from an actual increase in sales of the *Journal* and *Metallurgical Abstracts* of £960 and in advertisements of £449, offset, however, by a decrease in the sales of Special Publications of £728. Income from investments dropped only slightly, though their capital value suffered many vicissitudes during the year. The total net increase in income was thus £1222. There was, however, an increase in expenditure of £1767. The main increases were: (a) a rise of £1003 in salaries, wages, and national insurance, and (b) additional direct expenditure of £1598 on publication, due to the issue of larger volumes and the intrinsic increase in the cost of printing. Meeting expenses were lower by £303.

The deficiency between income and expenditure for this year is £1497, as compared with a deficiency of £864 a year ago. The figure of £1497 is obtained after allowing £489, the excess of income from the sale of Special Publications over their direct printing cost. The real deficit is therefore of the order of £2000, and it will be apparent that revenue must be substantially raised if the progress of the Institute is to be maintained and the budget balanced.

As on the previous occasion, the deficiency will be met by a transfer from the War-Time Emergency Fund, which will then stand at £3114. This will be further diminished to £2078 early in the coming year by a payment of £1036 for the first half of the 10-year index. This Fund has thus suffered a reduction of 73% in four years.

The net decrease in assets is £1401, made up as to a decrease in investments and funds of £839 and in the balance of current assets and current liabilities of £624, coupled with an increase in fixed assets of £62.

Publication of original papers and abstracts, of symposia, and monographs on particular subjects selected by the Council continue to be the principal activities of the Institute. The first is a continuing feature, while the two others are spasmodic, publication being decided upon as varying aspects of metallurgy appear to become increasingly important.

The sale of the Special Publications should not ordinarily be considered a possible source of regular income. They are a service to members from which it was never intended to make any considerable income above the actual direct cost. Owing to the irregularity of their issue, however, it may happen—as in the cases of Monographs Nos. 6 and 7—that there has been little time in which to realize the sales that may safely be predicted, although the expenses of preparation and printing have had to be met. An advantage to set against this disadvantage will be seen next year. As it is, there is an excess of income over expenditure in the Special Publications account of £489, giving an overall net excess of direct expenditure on all publications of £1175.

The sales of the *Journal* and *Metallurgical Abstracts* volumes are expanding, indicating the ever-widening appreciation of the Institute's work. This year they amounted to £5179, which is £960 in excess of last year's figure. The revenue received from advertisers at £5056 shows an increase of £449, and brings the total income on *Journal* account to £10,235. The direct expenditure

on the same account, however, was £11,899, £482 in excess of the estimate and some £1600 above last year's figure. This was due to: (1) the issue of larger volumes of the *Journal*, following the acceptance of a greater number of papers for publication; (2) larger increases in most charges, especially printing; (3) despatch costs to a larger membership; (4) enhanced costs of binding; and (5) expanding fees for abstracting.

An attempt has been made on this occasion to include separately in the accounts the direct and indirect salaries, superannuation, and overhead charges which are applicable to each type of publication, and thereby to assess on a reasonable basis the proportion of the expenditure which may be attributed to them and to the other activities of the Institute. There is no pretence of absolute accuracy in these allocations, but they give a fair picture of the total income and the way in which it is spent. Thus, on this basis, of a total expenditure of £27,082 during the year, £24,435 or 90% was spent on publications, and only £2647 or 10% on the remaining activities. On the other hand, members' subscriptions were only £12,180 or 47% of the total income of £25,585, the remainder being made up by sales of publications and advertisement space—£12,146 (47%), and by interest from investments—£1259.

It is very satisfactory to know that revenue from advertisements during the year exceeded the estimates by £257 and the total for 1948-49 by £449 (9.7%).

At the end of June 1950 the large sum of £585 was outstanding in unpaid subscriptions, but much of this has since been recovered or can be accounted for. Emphasis is again laid on the helpfulness of paying subscriptions promptly, either by Banker's Order or in the first week or two of the financial year, so that the normal expenses of the Institute may be met as they arise.

It is desirable that, in presenting the accounts for 1949-50, attention should be drawn to the provisional estimates for the ensuing year. Experience seems to show that, omitting any gains or losses from the issuing of Special Publications, the Institute is at present failing to balance its budget by approximately £2000. Moreover, the evidence is that this will be still further increased, since the Editorial Department is understaffed and all costs, particularly those of publication, are still rising. If the Institute is to maintain its present range of activities at a consistently high level, and also to add to the services it renders to its members, an increase in income of at least £5000 per annum will be needed.

The Council has concurred in, and supported wholeheartedly, the President's appeal to industry for contributions towards this objective. Some assistance will probably be derived from an increase in advertising revenue, in the obtaining of which many members could play a helpful part, but in the main the current hope must be that the non-ferrous industry will recognize the part the Institute is playing in providing the forum for the presentation and discussion of a continually expanding volume of original research to which all members—and indeed anyone—may refer in order to advance the production and efficiency of the products in which they are particularly interested. The greater benefit to be derived from publication does not accrue to the authors but to the industry as a whole, be the individual firms represented in the membership or not. It is therefore hoped that those firms in the industry who, directly or indirectly, profit from the policies pursued by the Institute will show their recognition by substantially supporting the present appeal. The degree of response from industry will be a measure of its appreciation of the increasing influence and usefulness of the Institute and will correspondingly stimulate or retard its progress.

THE INSTITUTE OF METALS.

SCHEDULE OF SECURITIES, 30 JUNE 1950.

30.6.49.	£	£		£	s.	d.	£	s.	d.
			<i>General Fund :</i>						
	5,500		£5,500 3% Savings Bonds, at cost . . .	5,500	0	0			
	1,010		£1,010 2½% Treasury Stock, at cost . . .	1,010	0	0			
	4,734		£4,359 4% Consolidated Stock, at cost . . .	4,734	6	11			
	5,057		£5,000 2½% National War Bonds, at cost . . .	5,057	1	0			
16,301							16,301	7	11
			<i>Endowment Fund :</i>						
	525		£525 2½% Defence Bonds, at cost . . .	525	0	0			
	1,285		£1,285 3% Savings Bonds, at cost . . .	1,285	0	0			
	19,482		£17,926 4% Consolidated Stock, at cost . . .	19,482	7	4			
21,292							21,292	7	4
			<i>War-Time Emergency Fund :</i>						
	500		£500 2½% Defence Bonds, at cost . . .	500	0	0			
	375		£500 15s. War Savings Certificates, at cost . . .	375	0	0			
	150		£150 £1 War Savings Certificates, at cost . . .	150	0	0			
	950		£950 2½% National War Bonds, at cost . . .	950	0	0			
	880		£795 4% Consolidated Stock, at cost . . .	880	0	0			
2,855							2,855	0	0
£40,448							£40,448	15	3

THE INSTITUTE
BALANCE SHEET

30.6.49.

£	£	£	£	s.	d.	£	s.	d.
			RESERVES.					
	21,295		<i>Endowment Fund</i>	.	.	21,294	9	10
	10,000		<i>General Reserve</i>	.	.	10,000	0	0
	4,473		<i>Entrance Fees</i>	.	.	4,478	3	5
35,768								35,772 13
			CURRENT SURPLUSES.					
			<i>Accumulated Fund:</i>					
	3,026		Balance as at 30 June 1949	.	.	2,776	11	7
	864		Amount transferable from War-Time Emergency Fund	.	.	1,497	8	3
3,890						4,273	19	10
						£	s.	d.
	864		Less Excess of Expenditure over Income for the year	.	.	1,497	8	3
	250		Transfer to Investment Redemption Reserve.	.	.	250	0	0
1,114						1,747	8	3
2,776						2,526	11	7
	5,383		<i>War-Time Emergency Fund</i>	.	.	4,611	2	3
	864		Less Amount Transferable to General Funds	.	.	1,497	8	3
4,519						3,113	14	0
750			<i>Special Publications Reserve</i>	.	.	750	0	0
500			<i>Investment Redemption Reserve</i>	.	.	750	0	0
8,545								7,140 5
			CURRENT LIABILITIES.					
	3,499		Sundry Creditors	.	.	1,184	17	11
			Lloyds Bank, Ltd.	.	.	1,851	6	11
	411		Subscriptions in Advance	.	.	1,188	7	1
3,910								4,224 11
			SPECIAL FUNDS.					
	16,846		<i>Mond Nickel Fellowships Fund</i>	.	.	20,557	9	5
	258		<i>Copper Pass Fund</i>	.	.	316	1	3
17,104								20,873 10

REPORT TO THE MEMBERS OF THE INSTITUTE OF METALS

We have audited the above Balance Sheet dated 30 June 1950, and the annexed Income and Expenditure Account for the year ended 30 June 1950, and report that we have obtained all the information and explanations which to the best of our knowledge and belief were necessary for the purposes of our audit.

In our opinion, proper books of account have been kept by the Institute, so far as appears from examination of those books.

The above mentioned Balance Sheet and annexed Income and Expenditure Account are in agreement with the books of account. In our opinion, and to the best of our information, and according to the explanations given us, the said Accounts give the information required by the Companies Act 1948, in the manner so required and give a true and fair view, in the case of the Balance Sheet of the state of the Institute's affairs as at 30 June 1950, and in the case of the Income and Expenditure Account of the excess of Expenditure over Income for the year ended 30 June 1950.

POPPLETON & APPLEBY,
CHARTERED ACCOUNTANTS,
BIRMINGHAM AND LONDON.

13 September 1950.

Approved on behalf of the Council:

H. S. TASKER, *President.*W. A. C. NEWMAN, *Honorary Treasurer.*C. J. P. BALL, *Chairman, Finance and General Purposes Committee.*S. C. GUILLAN, *Secretary.*£65,327£68,011 1

METALS.

30 JUNE 1950.

£	£		£	s.	d.	£	s.	d.
6.49.								
		FIXED ASSETS.						
		<i>Office Furniture and Equipment :</i>						
	1	Nominal value as at 30 June 1947				1	0	0
	401	Additions since, at cost				579	18	7
	402					580	18	7
	93					209	9	5
309		<i>Less Depreciation to date .</i>				371	9	2
		<i>Library Books, &c. :</i>						
1		Nominal value as at 30 June 1947				1	0	0
310						372	9	2
		INVESTMENTS AND FUNDS.						
		<i>General Fund :</i>						
	16,301	Securities at cost, per schedule				16,301	7	11
	67	(Market value £15,469 6s. 7d.)						
16,368		Deposit				—		
		<i>Endowment Fund :</i>						
	21,292	Securities at cost, per schedule	21,292	7	4			
	3	(Market value £20,044 5s. 11d.)						
21,295		Lloyds Bank, Ltd., Deposit Account	2	2	11			
			21,294	10	3			
		<i>Less due to General Fund .</i>				5		
						21,294	9	10
		<i>War-Time Emergency Fund :</i>						
	2,855	Securities at cost, per schedule	2,855	0	0			
	25	(Market value £2,786 16s. 7d.)						
	476	Lloyds Bank, Ltd., Deposit Account	25	5	2			
	504	Post Office Savings Bank	231	0	5			
	534	London Trustee Savings Bank	516	15	4			
	954	Lloyds Bank, Ltd., Current Account	15	10	11			
	35	Payments in advance for publica- tions	656	10	4			
5,383		Sundry debtors	311	0	1			
43,046			4,611	2	3			
						42,207	0	0
		CURRENT ASSETS.						
	1	<i>Publications, at nominal value .</i>				1	0	0
	489	Debtors: Subscriptions	585	3	1			
	50	<i>Less Provision for doubtful subscrip- tions .</i>	75	0	0			
	439		510	3	1			
	2,652	Sundry debtors and payments in ad- vance.	3,996	12	1			
3,091		W. H. A. Robertson Fund	29	13	6			
	12		4,536	8	8			
	1,763	Cash in hand	20	12	11			
1,775		Cash at Lloyds Bank, Ltd.	—					
4,867						4,558	1	7
		INVESTMENT OF SPECIAL FUNDS.						
		<i>Mond Nickel Fellowships Fund :</i>						
	5,000	Abbey National Building Society	5,000	0	0			
	1,250	Halifax Building Society	3,250	0	0			
	1,250	Co-operative Permanent Building Society	1,250	0	0			
	1,008	Post Office Savings Bank	1,528	6	6			
	1,007	London Trustee Savings Bank	1,526	4	4			
	4,088	Lloyds Bank, Ltd., Deposit Account	4,765	15	5			
	24	Lloyds Bank, Ltd., Current Account	7	10	3			
	3,150	Income Tax Recoverable	3,150	0	0			
	69	Interest Accrued Due	79	12	11			
16,846			20,557	9	5			
		<i>Capper Pass Fund :</i>						
	255	Post Office Savings Bank	311	1	3			
	3	Interest Accrued Due	5	0	0			
	258		316	1	3			
17,104						20,873	10	8
35,327						£68,011	1	5

INCOME AND EXPENDITURE ACCOUNT

		EXPENDITURE.			
30.6.49.	£	£	GENERAL ADMINISTRATION:	£ s. d.	£ s.
		871	Rent Services and Insurance	875 12 8	
		136	Lighting and Heating	151 11 4	
		70	Repairs and Renewals: Furniture and Equipment	114 4 8	
	6,945		Salaries, Wages, and National Insurance	7,947 14 10	
		570	Superannuation Fund	545 12 8	
		583	Postage Despatch and Telephone (<i>less</i> Receipts)	558 13 9	
		718	Printing and Stationery	645 11 10	
		109	Sundry Expenses	88 14 7	
		29	Bank Charges	20 13 6	
		53	Audit Fee	52 10 0	
		162	Professional Charges	225 19 0	
		317	Staff Travelling and Secretarial Expenses	240 10 10	
10,563					11,467 8
694			PENSIONS TO FORMER STAFF AND PAST SERVICE PREMIUMS		694 0
			MEETINGS, GRANTS, JOINT ACTIVITIES, ETC.:		
		111	Official Entertaining	75 17 1	
		394	Meeting Expenses, Net	90 12 3	
		500	Joint Library Contribution	500 0 0	
		231	Local Sections and Associated Societies: Grants, Programmes, Postages, and Travelling	298 9 7	
		125	Joint Committee on National Certificates in Metallurgy	125 0 0	
		50	Joint Committee on Metallurgical Education	50 0 0	
		25	Mond Nickel Fellowships Committee: Administration Expenses	25 0 0	
		24	Subscriptions and Presentations	58 8 8	
		97	Council and Committee Expenses	131 7 1	
1,557					1,354 14
357			BAD AND DOUBTFUL SUBSCRIPTIONS		153 13
46			List of Members		
72			DEPRECIATION: FURNITURE AND EQUIPMENT LESS RECOVERED FROM SALES		91 3
13,289					13,761 1
			LESS PROPORTION ATTRIBUTABLE TO PUBLICATIONS:		
	5,155		Direct Salaries, Superannuation, and Expenses	5,342 0 0	
	5,676		Indirect Salaries, Superannuation, and Overheads	5,772 0 0	
10,831					11,114 0
2,458			EXPENDITURE ATTRIBUTED TO ACTIVITIES OTHER THAN PUBLICATIONS.		2,647 1
			PUBLICATIONS:		
			<i>Journal and Metallurgical Abstracts:</i>		
		10,301	Production Costs (including binding, reprints, despatch, reporting, etc.)	11,899 5 3	
		4,294	Direct Salaries, Superannuation, and Expenses	4,334 0 0	
		4,773	Indirect Salaries, Superannuation, and Overheads	4,736 0 0	
		19,368		20,969 5 3	
			<i>Special Publications:</i>		
	1,725		Production Costs and Royalties	1,422 1 0	
		861	Direct Salaries, Superannuation, and Expenses	1,008 0 0	
		903	Indirect Salaries, Superannuation, and Overheads	1,036 0 0	
	3,489			3,466 1 0	
22,857			EXPENDITURE ATTRIBUTABLE TO PUBLICATIONS		24,435 6
£25,315					£27,082 7

METALS.

FOR THE YEAR ENDED 30 JUNE 1950.

		INCOME.							
£	£				£	s. d.	£	s. d.	
3,449.		SUBSCRIPTIONS AND DONATIONS						12,179	17 1
1,633									
		INTEREST ON INVESTMENTS:							
	490	General Fund	489	16 0
	775	Endowment Fund	768	16 11
1,265									1,258 12 11

		PUBLICATIONS:			
		<i>Journal and Metallurgical Abstracts:</i>			
	4,219	Sales, net			5,179 6 9
	4,607	Advertisements, less general charges			5,055 13 10
	8,826				10,235 0 7
		<i>Special Publications:</i>			
	2,639	Sales, net			1,911 8 11
1,465					12,146 9 6

88	Reserve not required	
864	<i>EXCESS OF EXPENDITURE OVER INCOME FOR THE</i>	
	<i>YEAR</i>	1,497 8 3
5,315		£27,082 7 9

THE INSTITUTE OF METALS.
FUNDS ACCOUNTS FOR THE YEAR ENDED 30 JUNE 1950.

ENDOWMENT FUND.

EXPENDITURE.		INCOME.	
£	s. d.	£	s. d.
30,649.		By Balance at 30 June 1949	21,295 9 10
To Transfer to General Funds: Investment Interest	769	" Interest on Investments and Bank Interest.	768 16 11
" Balance at 30 June 1950	21,295		
<u>£22,064</u>			<u>£22,063 6 9</u>

WAR-TIME EMERGENCY FUND.

£	s. d.	£	s. d.
864		By Balance at 30 June 1949	5,287
To Amount transferable to General Funds	1,497 8 3	" Interest on Investments and Bank Interest.	96
" Balance at 30 June 1950	3,113 14 0		
<u>£5,383</u>			<u>£4,611 2 3</u>

MOND NICKEL FELLOWSHIPS FUND.

£	s. d.	£	s. d.
4,008		By Balance at 30 June 1949	13,859
To Grants	3,361 6 2	" Donations Received	7,000
" Applicants Travelling Expenses	25 19 9	" Interest on Investments and Bank Interest.	173
" Printing Stationery and Postages	87 0 8		
" Bank Charges	3 10 11		
" Professional Charges	—		
" Balance at 30 June 1950	20,557 9 5		
<u>£21,032</u>			<u>£24,035 6 11</u>

CAPPER PASS FUND.

£	s. d.	£	s. d.
150		By Balance at 30 June 1949	200
To Grants	150 0 0	" Donations Received	200
" Balance at 30 June 1950	316 1 3	" Bank Interest	8
<u>£408</u>			<u>£408</u>

W. H. A. ROBERTSON FUND.

£	s. d.	£	s. d.
100		By Donation Received	100 0 0
To Cost of Medal	129 13 6	" Balance 30 June 1950 due to The Institute of Metals	29 13 6
<u>£100</u>			<u>£129 13 6</u>

SYMPOSIUM ON METALLURGICAL ASPECTS OF THE COLD WORKING OF NON-FERROUS METALS AND ALLOYS.

(Papers Nos. 1286-1290.)

PROFESSOR F. C. THOMPSON, D.Met., M.Sc., F.I.M. (Vice-President) (*Rapporteur*), introduced the papers and reviewed briefly some of the main points in them.

MR. W. C. F. HESSENBERG,* M.A. (Member), said that there was one consideration of a fundamental nature which was intimately linked with some of the topics referred to in the technological papers. In a tensile test on wire, the strain during uniform elongation was measured by comparing the diameter of the wire before and after straining, and the work done in effecting that strain calculated by multiplying it by the stress, having due regard to the fact that the stress changed continuously with the strain because of work-hardening. In imparting a similar deformation by drawing that procedure was not permissible, first because the wire might have undergone more strain in going through the die than was indicated by its change in diameter, and, secondly, because work must be done against friction between the wire and the die. The total work of drawing might be split up as follows :

$$W = W_k + W_k' + W_\mu,$$

where W_k was the work done in effecting a particular reduction in diameter on the tensile test, W_k' that done in effecting additional strains not indicated by the change in diameter, and W_μ the work done against friction. That three-fold nature of the work of deformation was inherent in all technological working processes where metals were shaped between tools.

In the case of dies of small angle, W_μ was the predominating factor, since there was a relatively large interfacial area between the metal and the die; in large-angle dies W_k' was the more important, because the flow of the metal through the die was such as to cause internal strains which did not contribute to the net change in shape. Between the two extremes there was a die-angle at which the work of drawing was a minimum, a fact well known to wire drawers. That was largely a matter of geometry, and it was quite easy to see that in the case of rolling, large-diameter rolls corresponded qualitatively to small-angle dies and vice versa.

Cook and Richards had referred to the work of Brick, Martin, and Angier. In their work on the rolling and recrystallization textures of binary copper alloys, those workers had found that the textures for copper and 70 : 30 brass were quite distinct, the change-over taking place at 5 at.-% zinc for the rolling texture and 1 at.-% zinc for the recrystallization texture. Alloys of copper with manganese, aluminium, arsenic, antimony, silicon, and tin all showed brass textures; alloys with nickel and cobalt showed only copper textures. The first group of elements, which formed the yellow alloys of copper, increased the electron : atom ratio of the solvent metal; nickel and cobalt, which formed the pink alloys, did not do so. These facts, taken together, had always seemed

* Deputy Director and Head of Mechanical Working Division, British Iron and Steel Research Association, London.

to him to be very suggestive, but he was not aware that they had ever been followed up.

He would like to add to the list of references that Cook and Richards had given a recent paper by Calnan and Clews,* who had attempted to derive the deformation textures in polycrystalline face-centred cubic metals under conditions of combined stress, such as occurred in rolling and wire drawing, from knowledge of the operative slip mechanisms. If this approach could be combined with Hill's theory of anisotropic deformation, an integration of the mathematical and metallurgical theories of plasticity might be in sight.

Mr. Davies had referred in his paper to automatic control of strip gauge, a technique which the British Iron and Steel Research Association was actively investigating. He himself believed that automatic gauge control was perfectly feasible in principle, and the problem was essentially one of devising suitable Servo-mechanical equipment to operate it. The difficulties involved were not as serious as those successfully overcome in the field of naval gunnery and aerial navigation, to mention but two of the well-established applications of Servo-mechanics. Of the need for automatic gauge control he had no doubt. The traditional procedure of watching the contact micrometer and making occasional adjustments to the rolls by power-operated but manually controlled screws was altogether too slow in relation to modern rolling speeds.

At the top of p. 523, Mr. Davies had referred to the idea of a pre-loaded mill. This was an ingenious idea, but at best could only succeed in making the housings of the mill effectively rigid. During rolling the rolls themselves underwent an appreciable reduction in diameter in the plane containing the roll axes, which might amount to nearly half the total spring of the mill. Unless the rolls themselves could be pre-loaded all round the periphery, which did not seem to be a very practical proposition, the maximum reduction in spring obtained by pre-loading was not likely to be much more than 50%.

In Section X of his paper, dealing with the properties of sheet in relation to deep-drawing and pressing behaviour, Dr. Jevons had omitted any reference to tolerances on thickness. He wondered whether Dr. Jevons would be prepared to add something regarding the dimensional accuracy desired in deep drawing strip and sheet.

MR. Å. G. HENTZ † (Member), in connection with Cook and Richards's paper, wished to contribute some observations concerning crystallite or block formation in originally homogeneous crystals, associated with the working of molybdenum in the incandescent-lamp industry.

Sintered rods of molybdenum (about $13 \times 14 \times 400$ mm.), produced by powder-metallurgy technique for subsequent drawing to wire, were swaged down to roughly 8 mm. dia., at a temperature of about 1200° C., which for the metal in question meant cold working. The working was of necessity done below the recrystallization temperature, because molybdenum would prove brittle at ordinary room temperature if recrystallization had occurred during this earlier stage. On the other hand, it was desirable that working should be carried out as little below the recrystallization temperature as possible, in order to reduce the internal stresses in the material so that they would not exceed locally the cohesion of the metal and thus increase the risk of cracking or eventual fracture. During swaging there was a successive dividing up of the original parent crystals in the sintered rod into smaller crystallites, with a slight deviation in orientation from the main crystals.

Fig. A (Plate LXXII) was a photomicrograph of the structure of a cross-section of a sintered rod, the average grain-size being about 30μ . The structure

* E. A. Calnan and C. J. B. Clews, *Phil. Mag.*, 1950, [vii], **41**, 1085.

† Metallurgist, A. B. Lumalampen, Stockholm.

after swaging to 8 mm. dia. was shown in Fig. B (Plate LXXII). The original crystals—the boundaries of which were distinctly discernible only here and there—now had an average size of about $15\ \mu$, in agreement with the reduction in area effected during the hammering of the rod. Most of these parent crystals, however, had been broken up into a number of smaller crystallites measuring about $3\ \mu$. The generation of such a block structure seemed to be governed by four factors: (1) the degree of cold working; (2) the temperature at which the rod was worked; (3) the size of the parent crystals; (4) the orientation of the parent crystals.

An increasing degree of cold working involved an increasing formation of crystallite structure. Further, a lower temperature of working seemed to contribute to a more marked block structure in the metal. With increasing size of the parent crystals, i.e. larger average grain-size in the sintered rod, the tendency for the block structure to develop was lessened. Fig. C (Plate LXXII) showed the microstructure of a cross-section of sintered rod with an average grain-size of about $50\ \mu$. Fig. D (Plate LXXII) illustrated the corresponding structure in this coarser-grained rod after being swaged down to 8 mm. dia. The occurrence of crystallites within parent crystals in Fig. D was considerably less pronounced in comparison with Fig. B; in other words, the parent crystals showed less tendency to subdivide; existing crystallites had a size of about $4\ \mu$. It also appeared from Fig. B that certain crystals did not exhibit any crystallite structure. The probability was that such crystals had a special orientation, and this was confirmed by the similar appearance of the etching pits in these crystals. It might be a question of crystals possessing the most favourable orientation as regards deformation in relation to the direction of working of the rod.

If this crystallite formation, which had been microscopically observed in connection with the swaging of molybdenum rods, was of the same nature as the corresponding phenomena in some other metals (mainly deduced from asterism in X-ray-diffraction patterns) then a striking feature was the size of the crystallites in molybdenum. They were about 100 times larger than the values reported for other metals investigated ($3\text{--}4 \times 10^{-5}$ mm., according to Wood and Rachinger, and others) and were microscopically visible. Might not this considerable difference in size between the crystallites be related to the temperature of cold working, and thus be attributable in the case of molybdenum to the high temperature obtaining at the formation of the crystallites during the hammering of the rods? Naturally, one could also imagine that the molybdenum crystallites visible under the microscope were in turn divided into still smaller submicroscopical units of the magnitude established for many other metals by means of X-ray diffraction.

MR. J. G. WISTREICH,* M.Sc. (Eng.), A.M.I.Mech.E., said that he would like to enlarge upon Dr. Cook and Dr. Richards's remarks about the textures of drawn wire. He was rather surprised at the statement that wire drawing was primarily a process of tension. It was true that, in order to draw a wire through a die, it was necessary to pull it, but the tension caused by the pull was smaller—often very much smaller—than the compression imposed by the die. Wire drawing, just as much as rolling, was a process involving not only tension but also compression. In those circumstances, it seemed astonishing at first sight that the texture of drawn wire should be different from the texture of rolled sheet, and the same as that of a wire pulled in a tensile test.

To one uninitiated in the subject, the idea at once sprang to mind that the distinction was not between drawing and rolling texture, but between wire

* Head of Metal-Working Laboratory, British Iron and Steel Research Association, Sheffield.

and sheet texture. This idea, he had discovered, was supported by a number of papers, and he would like to call attention to one in particular, by von Vargha and Wassermann,* in which the authors found that the same characteristic texture was present in the interior of all wires, whether drawn or stretched or rolled or swaged. They made the point that this texture was a function, not of the forces or of the particular process involved, but rather of the symmetry of deformation. The story was quite different when it came to the surface of the wire. These two authors had demonstrated very beautifully the difference between the surface textures of drawn and rolled wire. It

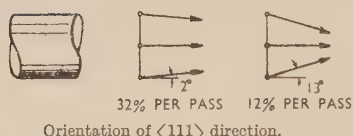
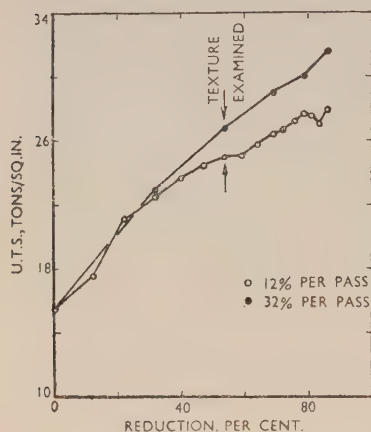


FIG. E.—Showing Effect of Drafting on Ultimate Tensile Stress of Annealed Copper Wire. (Wistreich.)

not of drawing and rolling textures, but of wire and sheet textures, and these referred to the interior of the material. Broadly speaking, these textures were determined by the symmetry of the deformation; the actual technological process left its distinctive mark on the surface of the product, and it appeared from the evidence cited that in wire drawing the reduction per pass was an important factor.

Wire-makers, especially in the steel industry, were familiar with the fact that heavy drafting produced a wire with a higher U.T.S. than light drafting. It was generally believed that this was due to strain-age-hardening, because it was well known that in heavy drafting the wire became much hotter. However, he had observed the same effect when steel wire was drawn very slowly, and also in copper wire.

appeared that the surface texture was markedly dependent on the geometry of the shaping process.

In some experiments which formed part of a wider programme of wire-drawing research, Mr. Wistreich said he had recently had occasion to examine the textures of two copper wires given about 54% total reduction by drawing, with this difference, that one of them was lightly drafted, i.e. the reduction per pass was about 12%, and the other was heavily drafted, the reduction per pass being about 32%. The following points emerged.

The familiar wire texture was present in the interior of both wires; that is, the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions were parallel to the wire axes. On the surface, however, the two wires clearly differed. In the heavily drafted wire the $\langle 100 \rangle$ direction was still parallel to the axis and the $\langle 111 \rangle$ was inclined at not more than 2° ; in the lightly drafted wire, on the other hand, the $\langle 100 \rangle$ direction was inclined at 10° and the $\langle 111 \rangle$ at 13° .

He concluded, therefore, that the terms describing textures in cold-worked metals should be more closely defined. One should speak

* G. von Vargha and G. Wassermann, *Z. Metallkunde*, 1933, 25, 310.

In one of the experiments mentioned annealed copper wire of just under 16 tons/in.² U.T.S. had been drawn in two lots, (12% reduction and 32% reduction per pass), the same dies being used where possible. After each pass the U.T.S. was taken, and as could be seen from Fig. E, after the initial cold work the difference in U.T.S. between the two wires emerged and eventually became quite pronounced.

In trying to explain this discrepancy in the properties of differently drafted wires in macroscopic terms, he had been faced with a paradox. According to the prevalent theory of drawing a light drafting involved a less homogeneous deformation than a heavy drafting. Baron and Thompson,* in a recent paper, had given a number of very good examples of that point. With less homogeneous deformation, one would expect a more work-hardened material. This was in direct contradiction to what had been found. It was then that the examination of textures described above had been undertaken. If one took into account this difference in texture, together with the known anisotropy of mechanical properties in copper, then, he thought, the observed influence of drafting on the mechanical properties of drawn wire was readily explained. He would also like to direct attention to the fact that the amount of cold work needed before this influence made itself felt coincided roughly with that which would cause formation of the texture.

In reply to a question by Professor O'NEILL as to whether there had been any special circumstances present in the reductions, such as heating, which had perhaps caused the drop in U.T.S. at a high total reduction, Mr. WISTREICH replied that these wires had been drawn very slowly by hand, so that heating was negligible. Whether there was any other factor operating, he could not say at this stage.

MR. E. C. LARKE † (Member) emphasized his belief that it was essential to the efficient development of the metal industry for the metallurgist to be fully acquainted with and appreciative of the work of the engineer who designed and provided the means of fabricating metals and alloys. In Mr. Davies's paper there was a dominating theme, namely higher rolling speeds, heavier reductions, greater widths, and heavier ingots; in brief, increase in production. Throughout the paper this theme was stressed, and it was important to remember the significance of this aspect of the subject.

With this in mind, he would like to consider the effect on output of delays which prevented metal from passing through the rolls, and to show, by means of a specific example, the extent of the rise in output due to increasing the roll speed and the coil length, both individually and together. The example he had chosen related to strip material rolled from 0.030 to 0.013 in. in three passes at a speed of 300 ft./min.; the speed had been raised to 600 ft./min. and the length of the coil doubled.

As would be seen from Fig. F, for a speed of 300 ft./min., 100 units has been taken as the maximum possible tonnage that could be rolled, representing the ideal output when the non-productive time was zero. The actual tonnage rolled, however, was 53 units, and the large difference was due simply to the influence of the non-productive time i.e. time during which the mill was running idle. Of the items responsible, general attention to the mill, both during the rolling of one batch of coils and before another programme of work was begun, amounted to about 50%. This item included, in addition, roll changing and general attention to the roll surfaces. Trouble due to mechanical breakdowns accounted for over 25%, and awaiting mill services a

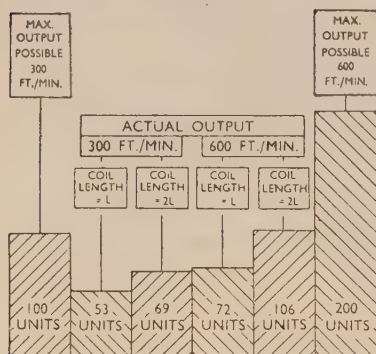
* H. G. Baron and F. C. Thompson, *J. Inst. Metals*, 1950-51, **78**, 415.

† Metallurgical Engineer, Research Department, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

little under 10%. It was worthy of note that electrical troubles accounted for only about 2½%.

If the speed was increased from 300 to 600 ft./min., the output rose only from 53 to 72 units. Doubling the length of coil had practically the same effect, namely 69 units as compared with 72. When the speed and the length were both doubled, the output rose to 106 units. It should, however, be noted that the effect of doubling the speed was to double the ideal output, and hence 106 units should now be compared with the maximum possible value of 200 units.

This example clearly showed that neither doubling the rolling speed nor doubling the coil length was very effective in increasing output. To achieve a significant increase it was necessary to double both the speed and the length.



Strip reduced from 0.030 to 0.013 in. in three passes.

FIG. F.—Showing Effect on Mill Output of (1) Lost Time; (2) Weight or Length of Coil; (3) Rolling Speed. (Larke.)

An equally important point which emerged was the urgent need to consider ways of reducing non-productive time, since this factor alone was responsible for the fact that the actual output was only about 50% of the maximum possible output.

He would like to suggest that all firms engaged in the rolling of metals should inaugurate a system whereby the causes responsible for the idle running of plant were systematically tabulated and analysed. Each firm naturally endeavoured to eliminate these troubles itself, but it would be of great value if the mill maker were advised of the results of such systematic observations. The information would be of advantage in future design, both of individual mills, with their complex auxiliaries, and of the plant employed for general mill service; while those

responsible for the conception of schemes involving the operation of inter-dependent rolling units would be in a sounder position to provide a balanced production unit.

He would welcome Mr. Davies's opinion as to the limitations of a powerful four-high mill engaged in the rolling of single sheets. His own experience had been the same as that noted by Mr. Davies, namely, that the extent of the reduction was limited by the necessity to avoid negative spread at the back end of the sheet. A skilled sheet roller using what was known as a mangling mill (a simple two-high mill engaged on finishing) always grasped the back end of the sheet and forced it upwards against the surface of the top roll. He had been most interested to see the illustration of the "billy-roll", but surprised to read that it was not in general use in this country. The purpose of this device was obviously an attempt to transpose a trick developed by the roller into a mechanical operation, and he imagined that its application to a powerful four-high mill would reduce negative spread towards the back end of the sheet and make heavier reductions possible.

MR. W. A. FOWLER* (Member) said that he would like to congratulate Mr. Davies on facing up to what were still regarded as controversial issues by

* Production Manager (Manufactured Materials), The British Aluminium Co., Ltd., London.

many people, namely, the relative merits of the two-high versus the four-high mill, the tandem versus the single-stand mill, and the reversing versus the non-reversing mill.

Mr. Davies had referred, under the heading of gauge control, to the mill of the future, where the roll gap could be set under a pre-load in excess of the maximum required for any reduction. He thought that Mr. Davies had in mind the application of a load such as would compensate for the housing stretch and thus eliminate the effect of this variable on gauge. At first sight this sounded quite attractive, but he recalled, when watching the efforts of operators to control gauge on a four-high tandem mill, being impressed by the number of possible variables with which they had to contend. For example, there was the question of speed. A variation during any one pass could markedly affect the gauge, particularly when comparing the extreme of slow threading with the full running speeds of the mill. Strip tension also had a bearing on this matter, since, if it were necessary to vary tension to compensate for any irregularity in strip shape, the gauge inevitably suffered. A variation in thickness down the length of the stock could also prove an important factor and, as was well known, variation in the distribution and/or quantity of the lubricant could have similar effects. Finally, of course, there was the important question of thermal camber. Any change in this due to overheating was disastrous, not only in its effect on gauge, but also on strip shape. No doubt the pre-set loading which Mr. Davies envisaged would look after certain of these variables, and it would certainly eliminate the important one of housing stretch, which permitted of a variation in gauge with any variation in thickness of the ingoing strip. All rollers would be most interested in any developments on the lines suggested by Mr. Davies, but the successful application of pre-set loading would not be the answer to all gauge-control problems, and the same care as at present would have to be exercised in other directions until all the factors involved were brought under more or less automatic control.

Mr. Davies had also referred to the use of cone decoilers, fitted either with hand-brakes or drag generators, but had made it clear that brakes were fitted to provide light back tension only. It was very necessary, in the case of aluminium rolling, to keep this fact in mind, as any attempt to use the cone decoiler as a back-tensioning device invariably resulted in interface slip between the layers of the coil, which gave rise to minute though objectionable surface tears. These could persist throughout the subsequent rolling stages to the finished sheet. The only safe way was to instal between the cone decoiler and the rolls an independent means of achieving back tension, such as the use of bridles or, on the slower-speed mills, the use of substantial press boards. What must be avoided was a direct tensioning of the strip by means of the cone decoiler only.

With reference to Mr. Davies's comments on roll cooling and lubrication, he might instance an experience The British Aluminium Co. had had some few years ago with a two-high medium-speed strip mill, which was not externally flood-cooled. It was found, with the heavier coils with which they were dealing, that the thermal camber developed during the pass resulted not only in a fairly wide gauge variation, but in badly shaped strip. The cure at the time was to reduce the speed of rolling to a point at which the roll temperature became more or less stabilized. Although in some measure successful, this had, of course, a most adverse effect on rolling costs. It was decided, therefore, to reduce the camber to about half the value previously used, in order mainly to improve strip shape, and they were quite prepared to accept, say, three passes as being necessary where previously two were employed. What was found in practice, however, was that it was possible to run the mill at full speed and with the same reductions as previously and under much cooler

conditions. In addition, gauge control and strip shape were excellent. The explanation was thought to be that the higher peripheral speed encouraged a readier flow of oil into the bite and also shortened the time the lubricant was under pressure. Conditions were thus created more favourable to the retention of the film strength of the oil, the net result being to reduce the friction at the roll/strip interface. Whatever the reason, the improvement was quite outstanding.

He had been most interested to read Mr. Davies's opinion on the use of four-high mills for single-sheet rolling. This had been tried in certain of their own works, but with not too great a success. Four-high mills had been found most useful for the intermediate stages of rolling but not for final finishing. The trouble was that to obtain a shape suitable for the after-treatment of flattening, the reductions per pass had to be confined to something much below the power capacity of the mill, and thus, although a uniform cross-section could be obtained with the four-high mill, the economics of single-sheet finishing were little, if any, more favourable than for a two-high mill. He himself thought that for the pure metal and the softer alloys results were better than for the medium-strength and strong alloys. It seemed with these latter that beyond a relatively small reduction per pass the distortion of the sheets was such that no after-process of flattening could retrieve them as acceptable commercial products. The conclusion had been reached, therefore, that for the medium and strong alloys at least, some tensioning of the sheet during rolling was essential. He would like to hear further from Mr. Davies on this point, and would particularly welcome some information on the relative reductions per pass of strip produced on a four-high mill with tension, as compared with the reductions per pass for single sheets produced on a similar mill. If, as he strongly suspected, the reductions for sheet must be much smaller, then a mill of less robust construction and with less power could be entertained for finishing single sheets.

MR. N. H. POLAKOWSKI,* Dipl.-Ing., stated that, in connection with the paper by Dr. Jevons, he proposed to deal with reversed deep drawing and with one or two of its direct implications.

Reverse (or inverse) drawing had been receiving increasing publicity in recent years, and Dr. Jevons's reference to this process was the third within the last six months.† All three writers had been unanimous in their opinion that the reasons for the superiority of this process over the orthodox, unidirectional drawing were not understood, at any rate not fully. He would suggest that the explanation was comparatively simple.

In Fig. G there was represented diagrammatically the re-drawing of a first-stage cup into the final shape both by the direct method (*b*) and also by the reverse method (*c*). It would be seen that in the unidirectional method (*b*) the wall of the cup was bent over the edge of the blank-holder, straightened out, bent over the lip of the die in the opposite direction to that of the first bend, and finally straightened out. It followed that the external layers of the pressed metal were first strained to some maximum amount in compression and later to the same amount in tension. There was, therefore, a complete reversal of plastic strain from (— max.) to (+ max.).

In the reverse method (*c*), the number of bending and straightening-out operations was the same as in (*b*) with the important difference that the two bends were in one direction only. Therefore, each external layer of the pressed metal suffered a deformation either from 0 to (+ max.), or from 0 to

* Research Student, University College, Swansea.

† *Times Rev. Ind.*, 1950, [N.S.], 4, (45), 20.

Sheet Metal Ind., 1951, 28, (286), 51,

(— max.). So far, this analysis was not new, since it had been made by Crane* in 1932 and by Morgan† in 1936, but it did not seem to be widely known.

In the arrangement shown in (c) the top face of the sleeve die was flat, thus involving two bends, but in commercial practice the top was uniformly radiused so that there was only one single bend followed by straightening out in the throat of the die, as shown in (d). The magnitude of plastic strain in the material bent over the lip of the die depended only on the sheet thickness : lip radius ratio, and it did not matter from the fundamental viewpoint whether each bend was over 90° , as in (b) and (c), or over 180° as in (d).

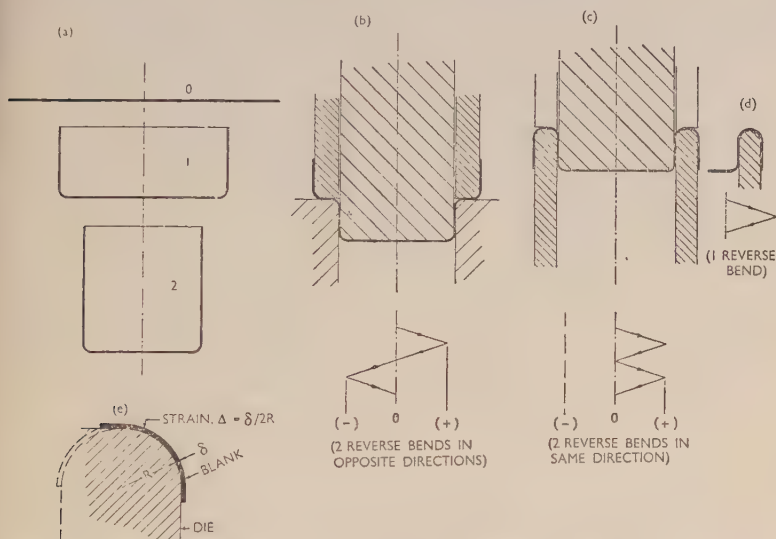


FIG. G.—Diagrammatic Representation of Re-Drawing of First-Stage Cup into Final Shape by the Direct Method and the Reverse Method. (Polakowski.)

The outstanding difference between the two drawing methods lay in the different sequences and amplitudes of bending during re-drawing and in their effect on the properties and behaviour of the pressed material. One must consider, therefore, the effects of large reversed plastic strains of varying amplitude upon the mechanical properties of ductile metals, and in particular on the residual ductility, both in the annealed and in the pre-stretched condition. In this way some information might be obtained on the conditions existing in the critical zone near the bottom of the pressing, where fracture was liable to occur.

In the experiments which he now wished to describe, reversed torsion had been employed as the most convenient method. Torsion had already been used by Professor Swift‡ in tests carried out with a view to applying the results to deep drawing. Moreover, collateral evidence indicated that reversed direct

* E. V. Crane, "Plastic Working of Metals and Power-Press Operations", p. 166. New York: 1932 (John Wiley and Sons, Inc.).

† H. E. Morgan, *Inst. Auto. Eng. Rep. No. 8601*, Class 81, 1936.

‡ H. W. Swift, *Engineering*, 1947, 163, 253.

strains, i.e. tension/compression, and reversed bending affected ductility in a qualitatively identical manner to reversed torsion.* Fig. H represented load/extension diagrams obtained on 63 : 37 brass wire $\frac{5}{32}$ in. in dia. Curve 1 related to the alloys annealed at 600° C. The steps bore a relation to the surface markings but were of no importance for the present purpose. Curve 2 represented a wire twisted four times forward and back over 540° ($1\frac{1}{2}$ revolutions each time) in one direction, as shown on the adjacent twisting schedule. Curve 3 was obtained when similar twisting was performed in both directions. The distance between the grips of the torsion machine was 8 in.

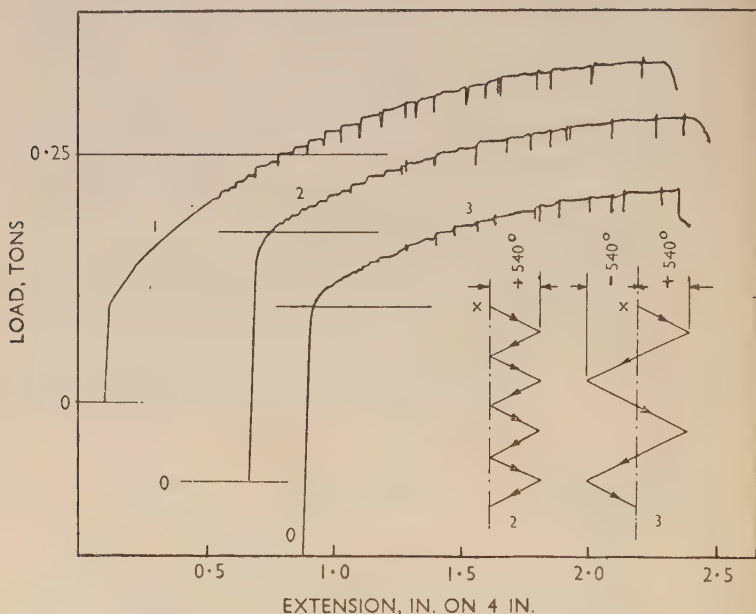


FIG. H.—Load/Extension Diagrams Obtained on 63 : 37 Brass Wire, $\frac{5}{32}$ in. in dia. (Polakowski.)

throughout. It was apparent that the residual elongation was much less in curve 3, the case relevant to direct drawing.

Fig. I showed results using 0.25-in. annealed rod of commercial aluminium (99.0%). Curve 1 applied to the annealed condition, curves 2 and 3 to rods twisted four times forward and back over 450° ($1\frac{1}{4}$ revolutions), in one and in both directions, respectively. Here again the residual ductility was less in curve 3, in spite of the fact that the overall amount of torsion imposed was the same in both instances.

The twisting schedules in these cases had been purposely doubled (i.e. more twists had been given than were required to imitate a single re-drawing operation). This had been done in order to bring out the differences more clearly. Curves 4 and 5 were obtained with samples first stretched 7.5% and

* G. Sachs, *Fracturing of Metals* (Amer. Soc. Metals), 1948, p. 51.
H. E. Morgan, *loc. cit.*, p. 51.

later given 360° twists by using alternate sequences. Here, also, it could be seen that sample 4 retained its ductility almost unaffected by torsion, whereas in 5 the elongation was small. The difference was still more accentuated when only the uniform elongations were compared.

Finally, Fig. J illustrated the behaviour of low-carbon steel (0.08% carbon) in similar tests. The curves marked "r" in rows (b) and (c), corresponded to commercial reverse drawing. Those marked "u" applied to unidirectional drawing. The differences in the values of uniform elongation were obvious in each case.

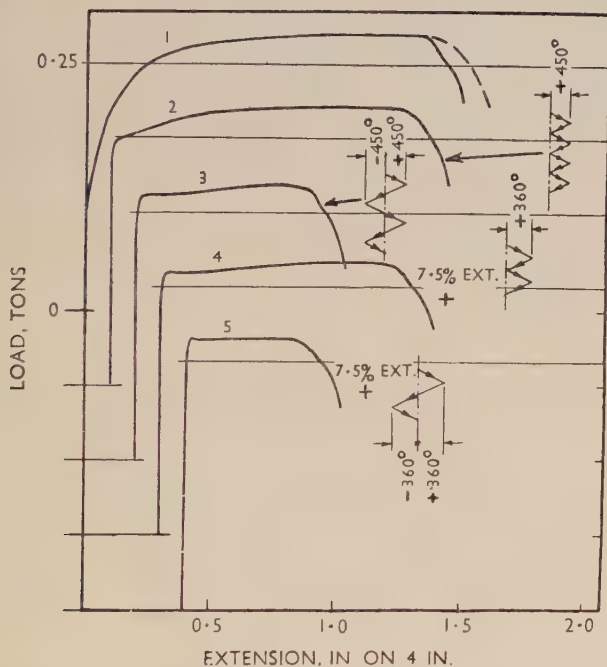


FIG. I.—Load/Extension Diagrams Obtained on 99.0% Aluminium Rod, 0.25 in. in dia. (Polakowski.)

These results demonstrated clearly the superiority of reversed drawing over the conventional method, and explained immediately why slightly larger blanks were required in the reverse process for the same end product. This was due to the large uniform extension, which involved much less thinning of the walls near the bottom of the cup than was the case in straight drawing. The results further supported Dr. Jevons's opinion regarding the usefulness of the general elongation value in assessing the possible drawing properties of a metal. True stress/strain curves would be useless for this purpose, since in each group illustrated in the figures an almost identical curve would be obtained in spite of the obvious differences in the uniform elongations. This was attributable to the fact that within fair limits both the fracture load and the reduction of area at the neck were little dependent on the

previous strain history of a ductile metal, as had been shown by Sachs,* by Swift,† and by Mehringer and MacGregor.‡

Finally, he would like to point out that the whole problem dealt with in his remarks seemed to be closely related to the more fundamental problem of fracture of metals under the action of repeated stress (fatigue).

With reference to Mr. Davies's paper, Mr. Polakowski said he would confine his remarks to the Section on "Gauge Control" (p. 522). In view of the

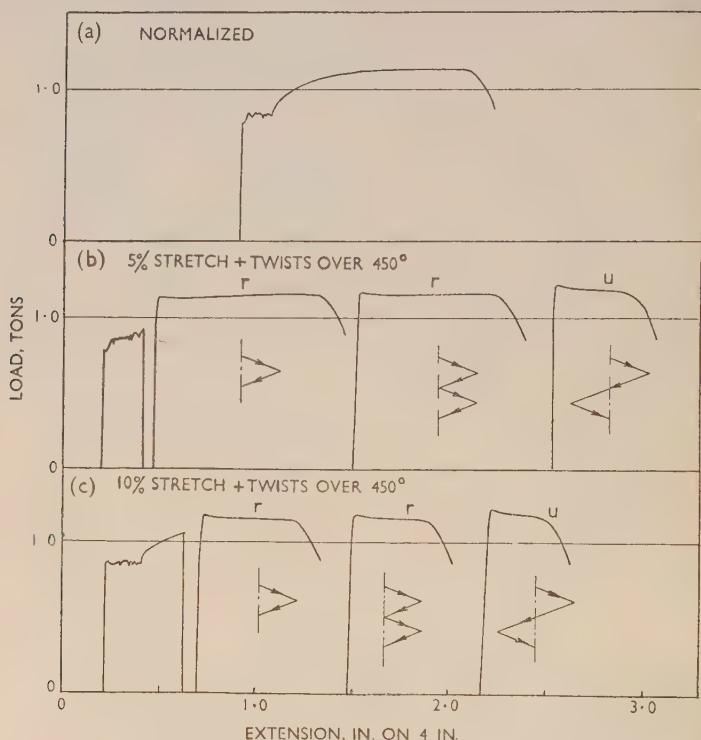


FIG. J.—Load/Extension Diagrams Obtained on 0.08% Carbon Steel.
(Polakowski.)

brevity of the description it was difficult to see what the author actually meant when he stated that a heavily pre-loaded mill should enable a very uniform gauge to be maintained. With regard to the effect of speed on gauge, this would persist whatever the initial pre-load. The effects of housing stretch on roll force could be eliminated by the application of a hydraulic roll loading (constant roll-load mill), but it could be shown on general grounds that such a mill would produce more off-gauge strip under otherwise comparable conditions than would a standard, screw-loaded mill.

* G. Sachs, *loc. cit.*

† H. W. Swift, *J. Iron Steel Inst.*, 1939, **140**, 181p.

‡ F. J. Mehringer and C. W. MacGregor, *Trans. Amer. Inst. Min. Met. Eng.*, 1945, **162**, 291.

The method used in high-speed tandem strip mills in the U.S.A. for keeping the delivery thickness as constant as possible consisted in bringing down the screws of the first stand when the gauge was becoming heavy. Simultaneously the tension was increased between stands 1 and 2, and in tinplate mills also between stands 2 and 3. In this way no excessive tensions were thrown upon the thin, hard, and brittle strip between the last stands, and excessive coil breakage was avoided. It was usually more convenient to operate the screws on the first stand than on the last, where the strip was very thin. This practice seemed to be a good one, and it could be applied to tandem trains rolling non-ferrous strip as well. So far this method was not automatic.

MR. A. B. ASHTON,* M.Sc. (Member), said that his remarks applied only to the drawing of copper and copper alloy wires on high-speed multi-die machines. He wished to consider these machines from the standpoint of lubrication. In the last analysis the purpose of the wire-drawing technologist was to enable machines to produce the maximum amount of wire at the minimum cost, and one found that lubrication, or features associated with it, played a large part in the economic picture.

In the old days of single-hole drawing, lubrication had been achieved by applying to the wire a pure (non-aqueous) lubricant such as tallow or rape oil. This material was chosen for its lubricating properties only, and the only other demand made of it was it should not induce discoloration of the copper by chemical action. The advent of the carbide die, however, and the consequent development of high-speed, multi-die drawing had introduced another requirement, namely, that of cooling, and it was this requirement which now dominated the whole picture of lubrication in wire drawing. The rate of heat generation in high-speed drawing was very considerable, and if the heat were not abstracted in some way and the wire, so to speak, drawn adiabatically, the wire would emerge from the machine—if it emerged at all—at such a temperature as to discolour by oxidation.

It was worth noting that the heat generated arose from three main sources :

(i) The heat of deformation of the metal itself. This was a physical characteristic of the metal and was not under the wire-drawer's or engineer's control.

(ii) Frictional heat generated at the wire/die interface and resulting in heating of both wire and die. This component of the total heat would depend directly on the effectiveness of the lubricant applied to the rubbing surfaces.

(iii) Frictional heat generated by "slip" on the cones or capstans. The amount of this component would depend on the amount of the slip, and if the latter were zero would itself become zero.

Accordingly, cooling had become a dominant consideration in wire-drawing machine design. Design had achieved it by applying the aqueous soap solutions referred to in two of the papers in the Symposium. The solution was applied copiously to the whole of the working parts of the machine—cones, wire, and dies; indeed, in some designs these parts were literally submerged in a bath of the solution. He wanted to suggest that lubricating properties had been sacrificed in the interests of cooling, and that attention should be devoted to the development of materials superior as lubricants to the soap solutions now used. The aim should be to find a lubricant that would maintain a condition of full fluid lubrication under the high pressures and speeds encountered in wire drawing. He doubted whether much progress could be made so long as a water base was necessary. He pictured as desirable

* Research Manager, Frederick Smith & Co., Manchester.

something with a film strength higher than was attainable in an aqueous solution.

In order to carry further this principle of improved lubrication, while still complying with the demand for cooling, it might be necessary to employ two separate fluids, for what was primarily a good lubricant might not be an efficient coolant. This consideration led to the following requirements, which were radical departures from existing principles of design :

(1) Provision of internally water-cooled capstans or cones. The capstans should be regarded as coolers which would abstract the heats of deformation and of drawing friction from the wire as it passed from one die to the next. They might be made from a material of high thermal conductivity.

(2) Provision of internally water-cooled dies and die brackets. Die-cases might be made of high-thermal-conductivity material.

(3) Provision of a means of applying a lubricant to the wires entering the dies. The high lineal wire speeds might necessitate applying the oil as an atomized spray.

The use of a superior lubricant at the wire/die interface would lessen the amount of heat to be dissipated. It could also be lessened, as mentioned earlier, by reducing capstan slip to zero. This could be achieved by the adoption of infinitely variable speed drives to the capstans, so that the capstan speeds could be adjusted exactly to the drafting sequence. This principle had been experimentally developed on small machines in Germany and would be worth consideration for larger machines. Besides minimizing heat generation, it had the advantage of reducing capstan wear and, in his own opinion, would reduce the incidence of the fault in copper wire known as "block mark".

The consequence of improved lubrication between wire and die would be improved die life. Die life in itself was not very important, for die costs were a small fraction of the costs of wire drawing, at any rate in sizes drawn through carbide dies; but a consequence of improved die life would be a reduction of shut-down time for die changing, and that was something which was not negligible and not unimportant.

Mr. R. B. SIMS * said he would like to endorse Mr. Chisholm's view on the importance of strip lubricant in cold working. As the author had pointed out, the lubricant must possess several distinctive properties: it must be easily removable from the strip after rolling without staining the metal; its coefficient of friction must be stable under rolling conditions and should not be so small that the strip would not enter the rolls when taking a reasonably economic pass, nor so large that the surface of the strip was marked. It would be interesting to know what steps the oil manufacturers were taking to ensure that commercially available lubricants possessed these properties. The analyses of the rolling oils put on the market had never been disclosed, and it would be valuable to have this information for research purposes.

He did not think that for many years now there had been any doubt about the nature of the frictional forces in the roll gap. Slipping friction existed in the arc of contact in almost all cases when rolling strip at thicknesses below 0.1 in. Only where the roll diameter was very large compared to the thickness of the strip (and therefore the length of the arc of contact was very long in comparison with the thickness) was there any possibility of sticking between the rolls and strip, and then the neutral plane was transformed into a neutral zone. This condition could be calculated by Orowan's equations.†

* Head of Rolling Section, British Iron and Steel Research Association, Sheffield.

† E. Orowan, *Proc. Inst. Mech. Eng.*, 1943, 150, 141.

The paper brought forward a completely new idea of the relationship between the coefficient of friction in the arc of contact and the viscosity of the rolling oil. Orowan and Hoff* had shown that soluble oil, when diluted to one part in ten with water, gave a mean coefficient of friction of 0.06–0.07, but when used undiluted the value was 0.08–0.09; palm oil gave 0.07–0.08, and mineral oil 0.09–0.11. At first sight there seemed to be little correlation between viscosity and coefficient of friction.

One point of interest was that where the coefficient of friction was small the energy of rolling was reduced, but the strip was produced with a dull velvety surface, which was not desirable in normal practice. It would seem, therefore, that the industry was prepared to incur waste of mill power resulting from using a poor strip lubricant in order to obtain the surface finish it desired.

Mr. Davies had dealt briefly with mill spring, but did not mention its application to gauge control. The two-high experimental mill at Sheffield was an ordinary production mill which had been instrumented to form a research tool. It had been found by direct measurement on the mill that the rolls moved apart in the proportion of 1 in. for an applied load of 1910 tons. Moreover, it had been shown experimentally that the combined diameters of the rolls in the plane of the roll axes decreased proportionally by 1 in. for an applied load of 4050 tons. By difference, the component of the total spring due to the roll housing was 1 in. for 3610 tons load. It was clear, therefore, that even if the housing were of infinite strength, the total mill spring could not be reduced below the value of roll spring, which in the experimental mill contributed one-half of the total.

Mr. Hessenberg and he had recently shown† that the exit thickness, the load in the mill, and the initial gap setting could be related by an equation: $F = M(h - S_0)$, where F was the total load in tons, h the exit thickness in inches, S_0 the roll setting without load, and M the elastic mill constant ($= 1910$ tons in.⁻¹ for the experimental mill). The mechanism of gauge control followed immediately from this equation; for if F were held constant and the roll setting remained constant during the pass, then it followed that h must be constant.

This equation could be made the basis of two methods of automatic gauge control. In the experimental mill an annealed strip 0.052 ± 0.004 in. thick and 300 ft. long had been rolled with automatic gauge control, the mean exit thickness being held at 0.036 in. to within ± 0.0003 in. He would therefore say that automatic gauge control was possible, and indeed a pilot plant had been operated.

There existed in the rolled strip a gauge error which Mr. Davies had not discussed; that due to roll eccentricity. It was clear that if the rolls had a resultant eccentricity due to the method of grinding, or to eccentricity in the roll-neck bearings, then the effective value of S_0 varied periodically, and from the elastic equation of the mill the exit thickness would change correspondingly.

The rolls of the experimental mill had been ground carefully, yet the net eccentricity had not been reduced below -0.003 in. and $+0.002$ in. on the roll radii. He wondered whether the error was additive in four rolls, so that when using a four-high mill, periodic variations in gauge increased because of roll eccentricity.

He would like to add some remarks to those made by Mr. Hessenberg (p. 686) about the contact micrometer as used in the control of gauge. Some form of contact strip micrometer was necessary in setting up a mill, because from published literature the accuracy of the penetrative radiation gauges was no better than $\pm 2\%$, which came within the bounds of British Standard

* *B.I.S.R.A. Restricted Rep. MW/A/r/6.*

† W. C. F. Hessenberg and R. B. Sims, *Proc. Inst. Mech. Eng.* (in the press).

tolerances for the finished cold-rolled strip. During rolling, the operator could not achieve a close control of gauge. Apart from the fact that the response of the strip micrometer was slow, the operator's natural response-time was at best 0.3–0.4 sec. It could be shown from Servo-mechanism theory that with these lags, together with those of the normal mill screw-down, he would reach gauge by a series of over and under corrections, so that the exit strip would show sinusoidal gauge variations before the correct gauge was obtained. Alternatively, if the adjustment were slow there would naturally be a great deal of off-gauge strip.

Mr. Sims said he would like to take up Mr. Davies on one point where he thought he was in error, namely, his statement that the effect of back tension was not important. Earlier work had shown its importance, and recently data from the experimental mill at Sheffield had been given* confirming this. It had been shown that if a back tension stress equal to half the yield stress were applied, then the effect on load would be to reduce it by 25% approximately, which he thought a quite considerable figure.

MR. P. C. VARLEY,† M.B.E., T.D., M.A. (Member), said that his remarks were more in the nature of amplification of one or two points in Dr. Jevons's paper.

The first, in connection with the use of multi-punch presses, was the advantage of using the metal slightly warm when deforming it. Much better results had been obtained in laboratory tests after the presses had been working for a short time, probably owing to better distribution of lubricants. On occasion they had warmed up the tools in an electric furnace before putting them into the press to a temperature of 40° or 50° C. By the time they were installed they had cooled down to 30° C. and there was then little change in temperature as drawing proceeded.

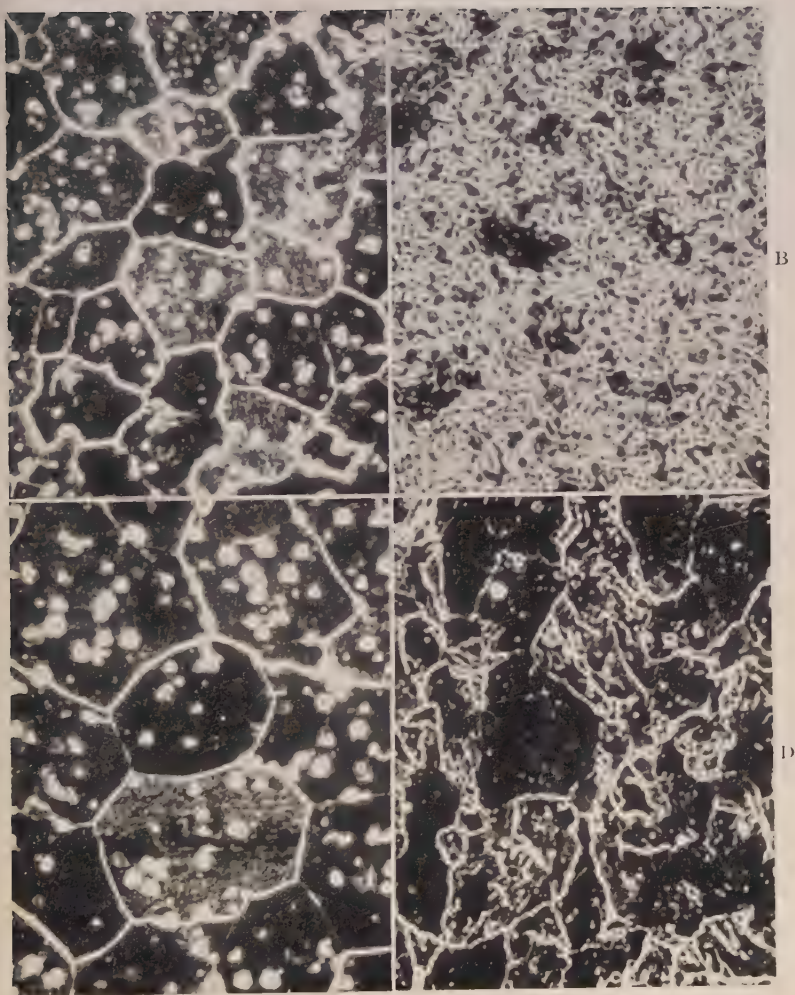
The next point was the importance of close temperature control in any inter-stage annealing process that the user might have to carry out. This was particularly necessary with a metal like aluminium, which was liable to grow large crystals if it were annealed after a critical amount of strain. In this connection he wondered whether the possibilities of a stress-relieving, or partial, anneal of, say, 1 or 2 hr. at 250° C. (for aluminium) had been explored. This would restore the ductility sufficiently to withstand subsequent deep-drawing operations, without any danger of the critical-strain growth.

Another point made by Dr. Jevons was that when drawing a cylindrical cup in aluminium, a deeper draw was possible with annealed sheet when using a punch with a hemispherical end than with half-hard or quarter-hard sheet, but that the opposite result was often obtained using a flat-bottomed punch. There was a further anomaly, in that the reductions obtained with the various tempers did not depend only on the form of the punch but also on the method by which the blank-holder pressure was applied. In tests at The British Aluminium Company's laboratories, using a spring-loaded blank-holder, the percentage reductions in the first operation were 50% with soft sheet and 49½% with half-hard. Using a blank-holder with what might be termed a positive clearance, i.e. where the distance between the holder and the face of the die was fixed by distance pieces, the corresponding figures were 49% and 51%. The difference had been confirmed with a large number of different batches of metal, and also for a variety of alloys as well as for the pure metal.

The condition of the tools was of vital importance. In some tests on an aluminium–2.5% magnesium alloy, carried out on a machine which permitted

* W. C. F. Hesseberg and R. B. Sims, *J. Iron Steel Inst.*, 1951, **168**, 155. R. Hill, *Proc. Inst. Mech. Eng.*, 1950, **163**, 135.

† Metallurgist, The British Aluminium Co., Ltd., Gerrards Cross, Bucks.



FIGS. A-D.—Photomicrographs Illustrating Influence of Grain-Size on Crystallite Formation in Sintered Molybdenum Rod. $\times 550$. (*Hentz*.)

FIG. A.—Fine grain-size (about $30\ \mu$).

FIG. B.—Structure after swaging rod to 8 mm. dia.

FIG. C.—Coarse grain-size (about $50\ \mu$).

FIG. D.—Structure after swaging rod to 8 mm. dia.

[To face page 700.



FIG. M.—Examples of (a) “Flamboyant” and (b) Ripple-Type Stretcher-Strain Marking Reproduced in B.N.F.M.R.A. Laboratory by Stretching Strip Specimens of Aluminium- $3\frac{1}{2}\%$ Magnesium Alloy. Approx. actual size. (*Eborall*.)

(a) Specimen stretched part way through initial yield. (Photo by *A. Loro*.)

(b) Specimen stretched approximately 15%.

measurement of the actual drawing load, a further polishing of the tools (already carefully prepared) in the direction of the metal flow had resulted in a reduction of the drawing load from 1.92 to 1.76 tons, with, of course, a corresponding increase in the size of the circle that could be drawn through the die. After being unused for several weeks, although the tools were carefully oiled-up to prevent rust and showed no deterioration of surface, the drawing load had reverted to the first value and they required repolishing.

MR. WISTREICH said that while he heartily endorsed what had been said about the distinction between lubricating and cooling, and the importance of the latter, he wished to draw attention to an important difficulty concerning the suggestion of die cooling.

At present no reliable measurements of the temperature at the die/wire interface were available. Measurements had been reported of the wire-surface temperature some distance away from the die, but it followed from theoretical considerations that this gave no indication of the temperature in the die. To illustrate this point he had calculated the wire surface temperatures at the die exit and some distance away from it for four cases of high-speed drawing. These were listed in Table A.

TABLE A.—*Calculated Temperatures in High-Speed Wire Drawing.*

Material	U.T.S., tons/in. ²	Reduction, %	Size, in.	Speed, ft./min.	Surface Temperature of Wire, °C.	
					At die exit	About 2 in. from die exit
High-Carbon Steel	85	27	0.080	1500	612	133
			0.040	2500	569	122
Copper	32	30	0.040	5000	134	59
				10000	166	59

Now, it had to be remembered that at these high drawing speeds the sojourn of the wire in the die amounted to no more than a few milliseconds. Consequently, the bulk of the heat generated by friction was carried away by the wire, and only a small fraction of it could be abstracted via the die. He concluded therefore that although the rate of heat transfer from wire to die might be somewhat improved by more thorough external cooling of the die, and possibly by suitable die design, even the most efficient cooling of the die could not altogether suppress the high die/wire interface temperature.

MR. D. A. BARLOW,* B.Sc. said he wished to comment on Dr. Jevons's paper, particularly as regards the deep drawing of aluminium alloys. The statement had been made that of the aluminium-magnesium alloys, the low-magnesium alloys behaved best under the press. He would suggest that this depended upon the type of operation and would not always be true.

Table B showed some results obtained with a hemispherical-ended punch on an experimental deep-drawing press, operated by a tensile-testing machine, similar to that used by Professor Swift.† Instead of a loaded pressure plate,

* Aluminium Laboratories, Ltd., Banbury, Oxon.

† H. W. Swift, *Inst. Automobile Eng. Research Rep., External Series No. 206*, 1940.

TABLE B.—*Deep-Drawing Tests on 20-Gauge Annealed Aluminium-Magnesium Alloy Sheet.*

2-in.-dia. hemispherical-ended punch. 50% radial clearance (i.e. no ironing).
Die rad. : 10 × sheet thickness. Blank-holder clearance : 0.002 in.

Magnesium, %	Max. Blank Dia. Punch Dia.	Elongation, % on 2 in.	Elongation, % on 8 in.	Erichsen No. : Depth of Cup, mm.
2	1.88	22	18	8.8
2.5	1.94	23	18	8.9
3.5	2.00	24½	19	9.1
7	2.06	28	24	8.2

a blank-holder giving a fixed clearance of 0.002 in. was used. This allowed the blank to flow freely, but prevented wrinkling. The drawability was measured as the ratio of the largest-diameter blank that could safely be drawn without fracture, divided by the punch diameter. It would be seen that as the magnesium content rose, the drawability increased. The elongations on 2 and 8 in. and presumably, therefore, the general elongation, showed a similar progressive increase. This might be expected, as the use of a hemispherical punch involved considerable stretching. However, the Erichsen value dropped for the 7% magnesium alloy in spite of the similarity between the types of test. The alloys were all produced under similar conditions, and results were repeatable.

TABLE C.—*Deep-Drawing Tests on 20-Gauge Aluminium-Magnesium-Silicide-Type Alloy Sheet.*

Composition : Cu 0.30, Mg 1.00, Si 0.54, Fe 0.35, Cr 0.22%.
Test conditions as in Table B.

Alloy Condition	Max. Blank Dia. Punch Dia.		0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elonga- tion, % on 2 in.	Erichsen No. : Depth of Cup, mm.
	Hemi- spherical Ended Punch	Flat-End- ed Punch, ¼ in. corner rad.				
Super-annealed .	1.88	2.06	4.7	9.3	18½	8.0
Freshly quenched (within 15 min.) .	1.88	2.06	5.4	12.1	22	7.8
Solution-treated and naturally aged .	1.81	2.06	11.7	15.1	15	6.7
Solution-treated and artificially aged .	1.75	2.06	15.9	19.0	11	6.2

Table C gave results of deep-drawing tests made on the same apparatus on a magnesium-silicide-type alloy. All blanks were cut from the same sheet and were given the appropriate heat-treatment. With the hemispherical-ended punch, the results roughly followed the trend of elongation and Erichsen values. It should be noted that the fully heat-treated material still offered a useful measure of ductility. Similar tests using a flat-ended punch gave a high value of drawability in each condition of heat-treatment. Contrary to the usual supposition, the fully heat-treated material had excellent deep-drawing properties in spite of the low elongation and high ratio of proof stress to ultimate stress. Fig. K gave the stress/strain curves for the alloy in the four conditions of heat-treatment. It would be seen that it was difficult to corre-

late tensile properties with the deep-drawing properties, especially as the latter depended upon the type of operation.

As Dr. Jevons has said, commercially pure aluminium often drew better in the cold-worked tempers than in the annealed or softest condition. Likewise, from the results shown, the softest temper might not always be the best, especially where a deep draw without ironing was required, using a flat-bottomed punch. However, where considerable ironing took place, as in the aluminium food cans illustrated in Fig. 12 (Plate LXVII) of Dr. Jevons's paper, Mr. Barlow said he had found that for a wide variety of aluminium-manganese, aluminium-magnesium, aluminium-magnesium-manganese, and aluminium-magnesium-silicide-type alloys, the softest condition and the softer alloys were preferable, in that the ductility remaining after ironing was greater, enabling flanging and, later, seaming of the can to be carried out with less danger of fracture.

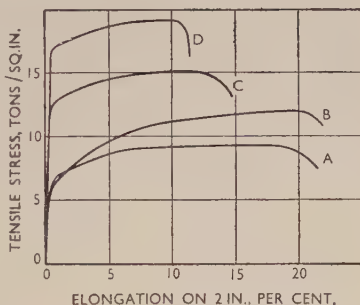


FIG. K.—Tensile-Stress/Elongation Curves on 20-Gauge Aluminium-Magnesium-Silicide-Type Alloy Sheet. (Barlow.)

- (A) Super-annealed. (B) Tested within 15 min. of quenching from solution heat-treatment. (C) Solution heat-treated and naturally aged for 3 months. (D) Solution heat-treated and artificially aged

MR. R. EBORALL,* M.A. (Member), wished to refer briefly to the paper by Dr. Jevons. On p. 603 this author had mentioned the formation of stretcher-strain markings in non-ferrous metals, especially in aluminium alloys, and in Fig. 8 (Plate LXV) had shown some rather striking examples of two types of markings. At the British Non-Ferrous Metals Research Association they were engaged in a study of this problem, and it had become apparent that there were two distinct features on the stress/strain curve corresponding to the two types of marking. In fact, in some aluminium alloys a definite yield point, similar to that found with steel, could occur.

Fig. L (a) showed a stress/strain curve typical of a material liable to give objectionable markings in the press shop, in this case aluminium-3½% magnesium alloy. The tensile machine was of the so-called "soft" type, for which yielding did not relieve the load, and the duration of the test was about 15 min. The first feature of importance was the relatively long discontinuous yield (A in the figure) at or near the start of plastic deformation, and this was responsible for the leaf-like type of stretcher-strain marking which Dr. Jevons called the "flamboyant" type (Fig. 8 (a), Plate LXV of his paper, and Fig. M (a), Plate LXXIII). The small step (A') was really a part of this same yield, but had prematurely taken place locally at one of the extensometer grips. The second feature was the series of small steps (B) (the Portevin-Le Chatelier effect †). The average elongation per step might become greater at larger total strains. Yields of this second type were responsible for the ripple-like markings shown in Fig. 8 (b) (Plate LXV) and Fig. M (b) (Plate LXXIII).

The curve in Fig. L (b) referred to an alloy of similar composition,

* Head of General Metallurgy Section, British Non-Ferrous Metals Research Association, London.

† A. Portevin and F. Le Chatelier, *Trans. Amer. Soc. Steel Treat.*, 1924, 5, 457.
A. W. McReynolds, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, 185, 32.

which had had different treatment, and showed the other extreme of behaviour. There was no distinguishable initial yield point of the first type; instead an appreciable amount of smooth plastic deformation occurred before the curve

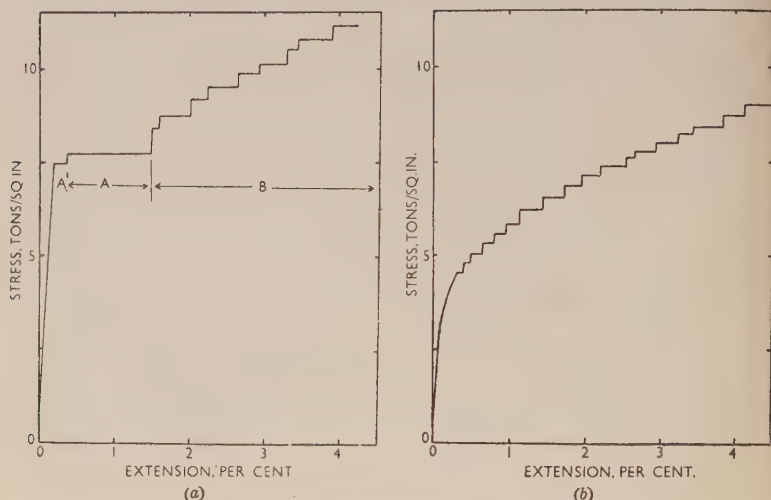


FIG. L.—Stress/Strain Curves for Aluminium-3½% Magnesium Alloy (a) Showing Yield Point and Steps, and (b) Showing Steps Only. (*Eborall.*)

developed a series of small steps which on the average increased in length as the total strain was increased. A material such as that would not show any markings of the leaf-like type when pressed. Ripples would appear on a heavily stretched strip, but they would not be easily detectable at the strains involved in most pressings.

Dr. A. T. CHURCHMAN,* B.Sc. (Student Member), pointed out that Dr. Jevons had suggested that scientists did not expect stretcher-strains in non-ferrous materials, as there were no yield kinks in the stress/strain curves of non-ferrous materials. However, as long ago as 1930 Sachs and Weerts† had reported a flat section in the stress/strain curve of gold-silver alloys and Schoenmaker‡ reported a small yield-point indication in copper and 72 : 28 and 60 : 40 brasses, which became more marked as the test temperature was lowered from 0° to - 80° C. Kuroda§ had tried to repeat these experiments, but failed. He had suggested that the kinks might be due to impurities in the alloys. An anomalous kink in the stress/strain curves of brass was recorded by Elam|| in 1927 and again in 1936.

Küntze¶ mentioned a yield elongation associated with a serrated stress/strain curve in Duralumin, the latter being reminiscent of the blue brittle

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† G. Sachs and J. Weerts, *Z. Physik*, 1930, **62**, 473.

‡ P. Schoenmaker, *First Communications New Internat. Assoc. Test. Mat.*, 1930, [A], 237.

§ M. Kuroda, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1938, **34**, 1528.

|| C. Elam, *Proc. Roy. Soc.*, 1927, [A], **115**, 148; 1936, [A], **153**, 273.

¶ W. Küntze, *Z. Metallkunde*, 1934, **26**, 106.

phenomenon in iron. This observation had been confirmed many times since, and recently Kê * had shown that internal-friction work on aluminium containing copper revealed a damping peak similar to that observed by Snoek † and by Dijkstra ‡ in iron containing small amounts of carbon and/or nitrogen.

Suspected yield points had been announced in zinc by Orowan § and in cadmium by Jenkins. ¶ A paper by Edwards, Phillips, and Liu in 1943 ¶ showed the existence of definite yield points in nickel containing 2.5% manganese, in standard silver, copper containing 1.85% beryllium, and Duralumin.

A definite yield point has been reported by Túry and Krausz ** in molybdenum that contained nitrogen. The yield displayed the characteristics exhibited by iron, namely, that the kink in the stress/strain curve could be removed by plastic deformation immediately before testing and could be restored by a low-temperature ageing treatment.

In the Metallurgy Department at Birmingham University a considerable amount of time had been spent investigating problems connected with the yield phenomena and it had been established that the characteristic yield phenomena were present in single crystals of zinc, †† cadmium, †‡ and α - and β -brass, when nitrogen was present in the material. Lüders bands had been observed in cadmium. He would venture to suggest that stretcher-strains in some non-ferrous materials might be eliminated by excluding nitrogen from the metal or by some addition to the metal which would fix nitrogen, as titanium fixed carbon and nitrogen in steel.

Dr. Jevons had suggested that Lüders bands in iron were observed only in fully annealed mild-steel sheet. This might be explained by an experimental observation at Birmingham on Armco iron. With grain-sizes finer than 200 grains/mm.², the fall in load at the onset of plastic flow and the yield elongation tended to be considerably smaller on ageing after plastic deformation than in the original fully annealed material. This had also been observed by Hall at the Cavendish Laboratory, Cambridge. The difference in plastic deformation between material in the Lüders band and the as-yet undeformed material outside the band would result in a less-marked band in the worked and aged material than in the virgin material.

This explanation might also account for the less-pronounced stretcher strains in the coarse-grained material. He himself and his co-workers had shown that the load drop at the yield point and the yield elongation decreased with increasing size of the grains, e.g. at 200 grains/mm.² the load might fall from 15 to 12 tons/in.² with an elongation of 2% or more, while in a single crystal of iron the load drop was very small and the elongation less than $\frac{1}{4}$ %.

Incidentally, the fact that the yield phenomena were so small probably accounted for various reports in the past that there was no yield point in iron single crystals.

MR. EDWIN DAVIS, §§ M.Sc., F.I.M. (Member), said that he would like to comment on certain of the metallurgical aspects of Dr. Jevons's paper as a supplier, not a user, of non-ferrous metals for press-work.

* T.-S. Kê, *Phys. Rev.*, 1950, [ii], 78, 420.

† J. L. Snoek, *Physica*, 1941, 8, 711.

‡ L. J. Dijkstra, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, 185, 252.

§ E. Orowan, [*Proc.*] *Internat. Conf. Physics*, 1934, (II), 81.

¶ C. H. M. Jenkins, *J. Inst. Metals*, 1931, 45, 307.

¶ C. A. Edwards, D. L. Phillips, and Y. H. Liu, *J. Iron Steel Inst.*, 1943, 147, 145P.

** P. Túry and S. Krausz, *Nature*, 1936, 138, 331; 1937, 139, 30.

†† H. L. Wain and A. H. Cottrell, *Proc. Phys. Soc.*, 1950, [B], 63, 339.

‡‡ A. H. Cottrell and D. F. Gibbons, *Nature*, 1948, 162, 488.

§§ Technical Officer, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

He was in sympathy with Dr. Jevons's plea for more co-operation between supplier and user, but too often the user did not know what was required. Dr. Jevons had emphasized the difficulty of assessing the suitability of sheet metal for press work from the results of the usual mechanical tests and metallurgical examination, but until the manufacturer of sheet received further information, he could do little to improve the situation. That meant more research into the fundamental aspects of deep-drawing operations, and although that was the field of those primarily interested in making deep-drawn products, the manufacturers of non-ferrous alloys would gladly co-operate.

It had been suggested by Dr. Jevons that 70 : 30 brass work-hardened less rapidly than 63 : 37 brass, but if the latter was free from β , as it was when supplied for deep drawing, then the differences in rate of work-hardening were negligible. For example, if both qualities were annealed to a hardness of 70 D.P.N. (diamond pyramid hardness number) then, after 50% reduction in thickness by cold rolling, the hardness of the 70 : 30 and 63 : 37 alloys would be between 170 and 175 D.P.N. and, after 80% reduction, between 210 and 215 D.P.N. In his reference to 80 : 20 brass for cold-drawing operations, Dr. Jevons had suggested that the alloy might be even more suitable if the grain-size were small, but sheet in that condition would be much harder than was usually considered acceptable. The hardness of 80 : 20 brass, annealed to give grain-size values of 0.02 and 0.01 mm., would be approximately 85 and 95 D.P.N., respectively, and similar values would be obtained on 70 : 30 brass treated to yield the same grain-size. Thus, from this aspect, there would appear to be little to choose between these two alloys. On the other hand, however, the rate of grain growth at annealing temperatures in excess of 650° C. was considerably less for 80 : 20 than for 70 : 30 brass, and, if intermediate annealing operations were effected at high temperatures, as was not unknown, then the final product in 80 : 20 brass might be more satisfactory than one in 70 : 30 brass similarly treated.

Dr. Jevon's reference to season-cracking, though brief, was very comprehensive, and there was little to add except emphasis here and there. Season-cracking was not confined to finished products, and in fact it was not uncommon for an intermediate product to be more susceptible to this type of failure than the completed article. Therefore, intermediate annealing of products with high internal stress should not be unnecessarily delayed if stress-corrosion cracking was to be avoided. Finally, it should be remembered that imposing stresses, either in assembly or in service, might render brass products susceptible to season-cracking, even though they were previously stress-relieved by annealing.

With reference to the use of multi-station machines, there was a very close analogy with the use of higher roll speeds. If one used a three-station press, one might expect to get three times the amount of work out of it that one would get from a single-station press, and from a twelve-station press twelve times as much. Those who dealt with multi-station presses knew only too well that that was not the case. If a single-station press broke down in a sequence of three operations, then only one-third of the capacity was out of operation. If one tool on a twelve-stage press failed, then the whole press was out of commission, and from the view point of production one such press certainly did not replace twelve single-station presses.

PROFESSOR H. FORD,* D.Sc. (Member), said that in the paper by Cook and Richards, he was interested in the reference to the previous work of those authors from which they concluded that there were two mechanisms of defor-

* Professor of Applied Mechanics, Imperial College of Science and Technology London.

mation, namely, slip within the crystals, followed by some general shearing mechanism. They had investigated in that case the cold-rolling process and had shown that the second mechanism became operative in the region of 50% reduction by rolling. In recent experiments he and his co-workers had been making plane plastic compression tests on high-conductivity copper. The material was compressed between two tools in such a way that it was deformed in plane strain. The deformation mechanism was therefore closely analogous to rolling. They had found some effect which they thought was probably connected with the mechanism described by Cook and Richards, but the statement on p. 469 of the paper might, if their findings were correct, be a little misleading as it stood, because the present tests had shown that the onset of the second mechanism could be delayed quite considerably by suitable pre-treatment of the material. In fact, in some tests it did not occur until about 80% reduction by plane compression.

On p. 470 there was a small point which he would like to have elucidated. The authors referred to the rolling process as being a process of compression and also of tension. While he agreed that if one applied external strip tensions, the tension stresses were applied up to the entry plane and beyond the exit plane from the roll gap, he did not see how tensile stresses came into consideration within the roll, except for small stresses at the edges of the strip. These could hardly be considered as being in any way major factors in deformation. He would like to know to what the authors were referring.

With regard to Mr. Chisholm's paper, he thought that the description of the mechanism of deformation in rolling was a little over-simplified in one or two respects. It was incorrect to suppose that there were two rival and contradictory theories of rolling. The question as to whether slipping took place over the whole arc of contact, or whether there might be a small zone where the roll and the material moved together, depended upon the geometry of the pass, the magnitude of the tangential frictional drag between the strip and the roll, and the yield stress of the material.

Mr. Chisholm had suggested that it was possible to have fluid-film lubrication in metal-working processes, and in particular in rolling. He himself thought it most unlikely that this could be achieved, or that that was the mechanism in the rolling process. The region was one of boundary lubrication—almost of solid contact—and although oil was carried through the roll gap, the lubricating film was probably never complete over the whole arc of contact.

Mr. Chisholm's paper gave the impression that viscosity was the most important factor in deciding the coefficient of friction in rolling. The tests by Orowan and Hoff, already referred to by Mr. Sims (p. 699), showed quite clearly that there was no simple connection between the coefficient of friction and viscosity. The effect of temperature on the properties of rolling oils had not been dealt with in the paper. Bearing in mind that there might be temperatures of the order of 200° C. or more in the arc of contact, it would seem that temperature might well be the most important factor in the choice of the properties of strip lubricants.

In general, the effect of lubricants in reducing the magnitude of the friction hill was of secondary importance in considering the suitability of lubricants in rolling. In other words, the reduction in the total power consumption was not great as between one lubricant and another. Strip lubricants were chosen for entirely different reasons, most of which Mr. Chisholm had mentioned.

Turning to Mr. Davies's paper, he would like to refer to the pros and cons of reversing as against non-reversing mills. Mr. Davies had set out all the main advantages and disadvantages, but one factor not included was the question of variation in thickness of the strip across the width. From time to time strip had to be rolled which was thicker on one edge than on the other.

After rolling, the difference in thickness would be reduced and could usually be brought within the accepted tolerances by the final pass. The non-reversing mill was under a disadvantage in this case in that, once having got the mill right for the first pass, the roll-adjustment was wrong for the second pass because the coil was turned over when it was taken back to the un-coiler, and the strip would not run straight without a side-to-side readjustment of the screw-down, even when tension was applied to the wind reel. In reversing mills, that difficulty did not arise, nor in the tandem mill.

He would also like to know whether Mr. Davies thought that in reversing mills the additional time taken in screwing down and in reversing the mill was much greater than the general man-handling of the coils in the non-reversing mill, even where it was possible to get a long run on a given batch of coils. His own experience at one steelworks had been that there was a distinct advantage in changing over to reversing.

Mr. Davies had mentioned only cooling by sprays. There were many mills in this country where cooling jackets were fitted to rolls, and he would like to have Mr. Davies's comments on their advantages and disadvantages. He himself believed that cooling by sprays, by flooding the rolls, was much the better method. Jackets had a tendency to pick up small particles which got stuck into the pads under the jackets, resulting in scratch rings round the rolls and on the strip itself. Mr. Chisholm had referred to the difficulties of cleaning when there was a circulating system for the coolant. He would like to have Mr. Davies's views on that subject, as his own experience had been that such cleaning could be carried out quite satisfactorily, and that the difficulties were not insurmountable, even if it was only possible to filter perhaps 20% of the total circulation.

MR. H. H. EGGINTON,* L.I.M. (Member), said that Dr. Jevons's paper might give the impression that the use of fine-grain 80 : 20 brasses in the 0.01-0.02 mm. grain-size range was rare, whereas they were used very extensively for deep-drawn parallel-sided tubes similar to those shown in Fig. 13 (Plate LXVII), particularly when such tubes were subsequently formed into flexible bellows for instrument and other purposes.

Such fine-grain brasses, which were ultimately drawn to wall thicknesses as low as 0.003 or 0.004 in. with a tolerance of less than a quarter of a thousandth of an inch, did exhibit, as had been pointed out, physical properties which conformed to the quarter-hard condition; but from the blank they cupped satisfactorily to 40-50% reductions and drew well to 20% wall reductions. They were also amenable to fairly rapid higher-temperature inter-stage annealing without grain difficulties, so that the fine grain was maintained throughout the cupping and drawing operations, and a wall of, say, 0.004 in. exhibited a reasonable number of grains through such a section, and a very fine surface, which was imperative for tubes subsequently fabricated into flexible bellows.

There were occasions when the brasses of gilding composition showed other definite advantages over brasses of the 70 : 30 type. A typical case was the production of an approximately 50% cup from a brass of 0.010 in. thickness with a blank of about 3 in. dia. The manufacture of such a cup in 70 : 30 brass was found to be difficult, owing to fracture of the wall, but was satisfactory in fine-grain brasses of gilding composition.

The advantages of the 80 : 20 and 90 : 10 brasses in such applications were, he thought, due to their lower work-hardening rate, for their ductility as measured by normal tensile tests was on the whole lower than that of

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70 : 30 brasses. As pointed out by Dr. Jevons, the gilding brasses also had a reduced susceptibility to season-cracking.

PROFESSOR H. W. SWIFT,* M.A., D.Sc., M.I.Mech.E., stated that he would confine himself to discussing two sections of Dr. Jevon's paper, testing (p. 591), and lubrication (p. 582).

Dr. Jevons had quite properly divided sheet-metal tests into three classes : common, special, and imitative. Among the common tests, he set most store on the ordinary tensile test and in particular on the value of "general elongation" at incipient necking. He claimed that "the information given by reasonably accurate stress/strain curves is most valuable", and "their results . . . can be used by men of experience to predict probable behaviour under the press", though "curves obtained by autographic recording methods are frequently on too small a scale to enable possibly important differences to be revealed with certainty".

There were three questions he would like to put to Dr. Jevons. Firstly, how could the tensile test be interpreted to give discriminating comparative information on drawability; secondly, what evidence of real correlation could be produced; and thirdly, how could it be applied as a reliable acceptance test?

On the other hand, Dr. Jevons discounted the value of true stress/strain curves because "the part in which they show the most difference from ordinary curves lies beyond the onset of necking, a condition which should not be reached in good deep-drawing practice". He himself affirmed with great confidence that in any reasonably deep single-stage draw the whole of the walls of the cup were subjected to a strain far greater than that which took place up to the necking point in an ordinary tensile test, in some cases to the extent of four times as much; so it stood to reason that a tensile test merely carried up to the point of necking with any material was not representative of the stress/strain relationship in the greater part of the deep-drawing operations.

Among the special non-imitative tests, Dr. Jevons had a kindly word for the wedge-drawing test, and suggested that "if its results were considered in the light of long industrial experience, it would prove to be not less informative, and probably more discriminating, than the tensile test". He had stated that workers in Sheffield, among others, had failed to find reliable correlation. Inspection of the article † to which Dr. Jevons referred would show that the failure was on the part of the test rather than of the investigators. In fact, at Sheffield, they had succeeded in proving fairly conclusively that there was a failure to correlate on the part of the wedge-drawing test; there was an inherent spread of 10% in results with a single lubricant and of 50% over a range of lubricants.

Again, among the imitative tests, Dr. Jevons had claimed that "hydraulic tests have the advantage that with the help of pressure and depth gauges a stress/strain curve can be plotted autographically". He would like to ask Dr. Jevons two questions : What was the stress that could be measured, and what was the strain? He challenged him to obtain an intelligible stress/strain curve from these measurements, even by laborious calculations, let alone autographically.

Dr. Jevons's criticisms of the cup-drawing test also were not altogether well informed. He had said "opinions differ as to what should form the basis of measurement and comparison" in such tests. He himself had not heard of any criterion except the maximum blank diameter from which a cup could be successfully drawn. Dr. Jevons also complained that with this test "for

* Professor of Engineering, Sheffield University.

† E. M. Loxley and H. W. Swift, *Engineering*, 1945, 159, 38, 77, 136.

every sample tested several blanks have to be machined accurately to different sizes", so that "tests of this kind must at present be regarded as being more appropriate to research than to the everyday acceptance testing of sheet under industrial conditions". In actual fact, all that was required for an acceptance test was a single blank of a prescribed diameter. Furthermore, Dr. Jevons quoted on p. 600 as a disqualification of this particular test the fact, which he had quite properly noted on p. 588, that anomalous results were obtained according to the form of pressing adopted.

Results obtained at Sheffield during the last two or three years showed that with aluminium and several of the aluminium alloys there was actually a double anomaly. Using a hemispherical punch with material which was fairly hard, the drawing ratio was small, and with soft material the drawing ratio was large. Using a flat punch, the position was the opposite; with the hard material it was possible to draw from a bigger diameter than with the soft material. So there was an anomaly between the hemispherical punch and the flat punch, and a further anomaly between hard and soft materials.

Other tests had proved that with brass and copper one of the anomalies existed, but the other did not. The drawability of soft metal was superior with the flat punch; with hard metal, the case was reversed. However, it was not shown, as with the aluminium alloys, that with a flat punch an improvement was obtained by using hard metal; in this case the hard metal did not draw as well as the soft metal in any circumstances.

But the presence of these anomalies in the cup-drawing test must not be held to disqualify it. Indeed, the fact that it was the only test that had revealed them proved that its powers of discrimination were superior to those of other forms of test, and was therefore a strong argument in its favour. Moreover, the undoubted fact that different metals had different orders of merit with actual pressings of different types was incontrovertible proof that no single test of any kind—drawing, cupping, or tensile—could possibly cover the whole range of drawability. But since the cup-drawing test was the only one obviously capable of making distinctions of the kind required, and that by means of quite simple modifications, it seemed a safer speculation for the future than any other form of test for drawability.

The Sheffield prototype of the press shown in Fig. 6 (Plate LXIV) of Dr. Jevons's paper was designed in 1940 to distinguish between pressings of the Erichsen and deep-drawn types and had subsequently been provided with hemispherical as well as flat-bottomed punches, so that it had gone at least some way to cope with the intrinsic complexities of the property known, but not yet understood, as drawability.

As regards lubrication, at Sheffield they had been endeavouring for a number of years to reduce the number of incommensurables that occurred in the problem of lubricant selection. Assembled numerical results of tests from the paper which Dr. Jevons had quoted as treating the subject "in general and often vague terms" proved that the effect of speed was not, as had been supposed, to reduce the friction under drawing conditions. With all the lubricants tested, the drawing load increased systematically and continuously if the speed was raised, more so with no lubrication or with a poor lubricant than in the case of graphite.

A series of tests,* in which Dr. Jevons's firm had very kindly co-operated, and in which certain cleansing processes and testing processes were applied to metal drawn with different lubricants, had shown that, curiously enough, graphite, either dry or with oil, did not appear to be more difficult to remove than some other lubricants. It had also been, perhaps, a little surprising to find that where considerable ironing took place, it was easier to remove the lubricant afterwards than where there was no ironing.

* B.I.S.R.A. *Research Rep.*, MW/E/11/50.

In conclusion, Professor Swift said that he sympathized with those in industry who were concerned to put lubrication on something like a scientific basis. So far as deep-drawing and similar problems were concerned, the selection of lubricants could not properly be based on a single criterion, but must rest on a combination of qualities, weighted according to circumstances. Certain of these qualities could be measured experimentally or compared by test, but others could only be judged by experience or by what, for want of a better word, one would call operational research. That particular side of the subject was one that could not be investigated in a University laboratory.

DR. R. SCHNURMANN* wished to raise a point in connection with Mr. Chisholm's paper concerning terminology. What was the physical meaning of the film strength of a lubricant and how could it be measured?

As regards the function of a lubricant under metal-rolling or wire-drawing conditions, Professor Ford had expressed the opinion that it was most unlikely that any hydrodynamic lubrication was involved. He agreed; and therefore it would appear that there was very little point in looking at the viscosity/pressure dependence of the lubricants. He believed that there was, as both Professor Ford and Professor Swift had said, certainly some point in considering the viscosity/temperature dependence. It appeared that the empirical result was that one required a lubricant of low viscosity and of a very steep viscosity/temperature curve.

He would like to ask Mr. Chisholm whether it was feasible that, at the exit side of the metal-working gear, where the pressure decreased very rapidly and the lubricant had ceased to act under "extreme-pressure" conditions, it was essential for the two parts—either the rolled strip or the drawn wire and the thickness-reducing appliance—to float apart, and therefore necessary to get as low a viscosity at that point as possible. Moreover, at the same time as that floating-apart took place, it was desirable to allow the lubricant to wash off the fines.

He believed the point had also been made that there was very little difference between various lubricants, but he himself thought that depended a great deal on the operating conditions. For instance, it did not matter very much whether one added a sulphur body, or a chlorinated body, or some French chalk, or any other "extreme-pressure" dope to a perfectly good mineral oil, but it was desirable to add something specific to it to prevent tearing, i.e. the plucking out of large particles from the solid bodies in frictional contact under "extreme-pressure" conditions or, at any rate, boundary-lubrication conditions.

When considering friction conditions in metal-working operations, one should not look only at the "coefficient of friction", since one never quite knew under what conditions it had been determined. When the "coefficient of friction" was a function of the applied load (outside the region of the validity of Amonton's law), it was essential to make sure that it was clear what the actual frictional forces were.

MR. C. E. DAVIES,† M.I.Mech.E. (Member), said that he would like to make a few remarks on Mr. Chisholm's paper, since he was very interested in the subject of lubricants from the point of view of rolling machinery and the rolling processes.

As Mr. Chisholm had stated, the selection of lubricants for cold rolling had in the past been determined largely by trial and error, and varied greatly in individual mills. The paper was welcome as an attempt to rationalize

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† Director, W. H. A. Robertson and Co., Ltd., Bedford.

practice. Unfortunately, as the author had himself emphasized, the desired characteristics in the lubricant depended on rolling conditions that differed in regard to speeds, reductions per pass, surface finish required, &c. In the case of brass, in the intermediate or "getting-ready" passes, where maximum reductions were wanted, a high degree of oiliness and viscosity would not seem to be so desirable, as the gripping power of the rolls would be reduced; the coefficient of friction between rolls and metal must be related to the contact angle.

In the United States the general practice was to apply a mixture of water and oil, flooded on to the rolls. This was a development of the old custom of immersing the coils in a tank, at the entry side of the mill, containing water on which a film of oil was floating. He believed that in the States the usual way of applying water and oil was by flooding the rolls with water and spraying oil on the strip as it entered the mill. It would be interesting to have opinions as to the value of this use of water to form the greater part of the lubricant; presumably the object was mainly to dissipate the heat generated in the pass and to spread the oily constituent. Rolling speeds were normally higher in America, but water was used on older mills running at speeds not greater than those now generally operated here. Soluble oil emulsion applied by spray or flooding should prove a very suitable lubricant.

In the case of finishing, a more oily lubricant was needed for several reasons; a lower coefficient of friction helped to ensure uniform elongation and to deliver flat strip, and—when rolling to light gauges—to reach the desired thickness in a minimum number of passes. It seemed probable that the necessity for dissipating heat existed even with moderate rolling speeds, say, 200–300 ft./min., if heavy reductions were taken in the finishing passes, particularly in four-high mills with relatively small work-roll diameters. Uniformity of roll temperature and maintained roll shape were essential, if gauge variation both in length of coil and strip width was to be avoided.

Lubricants for aluminium and its alloys presented other problems. Mineral oil of the type recommended by Mr. Chisholm had been successfully used, though it was common practice to dilute this with "white spirit" for finishing. In all types of cold rolling, distribution of roll lubricant and the method of application were almost as important as the exact nature of the lubricant itself. Patchy or irregular distribution was obviously bad. Incidentally, an efficient lubricant undoubtedly played a valuable part in preserving the surface condition of the rolls and reducing wear and the necessity of frequent re-grinding.

Generally speaking, oil specialists could develop and produce blended oils which would fulfil the requirements of the rolling industry within limits, but it was not easy to specify each and all of the desired characteristics of lubricants for each and all of the wide range of processes in the cold rolling of non-ferrous metals.

In connection with the paper on wire drawing by Cleaver and Miller, Mr. Davies said that he had noted with interest that apparently rotating dies were being considered and he would like to know whether there was any likelihood of practical progress being made in their use. He remembered that in about 1910 the old continuous cone-type machines were fitted with revolving dies.

MR. W. J. THOMAS * (Member) said that in the last 15 years there had been some amazing developments in the cold-working plant made available in this country, and he thought that was due essentially to the very much closer collaboration between the plant manufacturers and the plant users. There had been a time when the Continental plant manufacturers had things very much their own way, owing to their claims that they would not only supply a

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mill, or a piece of plant, but would put it into operation and ensure the output, and thus they acquired first-hand knowledge of production technique and problems—whereas for many years British plant manufacturers were not afforded the close collaboration which existed at present.

Many of the earlier mills installed for the light metal industry in this country were not well designed. He knew of many in which the ratio of roll diameter to length necessitated a camber something like a miniature Mount Everest, and these mills required a type of skilled operator able to control almost every foot of the strip as it was being rolled. The modern plants had, or at least should have, transferred a great deal of that skill from the operators to the plant designer and to the plant technical staff.

A very big change had followed the introduction of relatively friction-free bearings. The days had gone when the temperature of the strip as it emerged from the rolls was to a great extent due to the large amount of heat generated in the bearings and from which it was transferred into the strip. In those days the incidence of burns to the operators was almost an index of how efficiently the mill was working.

However, he thought it still remained a fact that a fundamental problem in cold rolling was the reduction of heat, whether it originated in the bearings or by the working of the metal in the rolls. The reduction of that heat, and the controlled dissipation of such heat as could not be avoided or which might even be advantageous, needed still further investigation.

It was very difficult for an operator to get a yard-stick which would indicate how efficiently the mill was working. One guide was the proportion of the R.M.S. rating of the prime-mover of the mill that was absorbed; how much of the power available to that mill was being taken away every hour? That was quite a good yard-stick, but in itself was not sufficient, as it might reflect the design as well as the operation of the mill. A much better criterion, to his mind, was what might be termed the roll efficiency. What proportion of the time or the distance travelled by the roll was really used?

The rolling efficiency taken over a week's operating on most mills was still an appallingly low figure. That was due to two factors: first, the design of the ancillary equipment for getting stock into and out of the mill quickly, and secondly the question of interruptions. Many of these had engineering origins, but there were still quite a number of metallurgical causes. He would instance, particularly, the question of roll-surface maintenance, flow marks, and other defects which developed during rolling, and which not infrequently necessitated the roll being changed because of some metallurgical defect.

Professor Ford had raised the point whether it was better to have a reversing mill or a single-pass mill. That would depend entirely on the operation to be carried out. The reversing mill might justify itself in some cases, but he thought that, in general, except for small jobbing mills, the single-pass mill had much to commend it.

MR. R. LINFORD * said that mill builders welcomed the modern trend of co-operation between the builder and the user.

He wanted to deal with a point which Professor Ford had mentioned, namely, that if strip thicker on one edge than the other was rolled on a non-reversing mill, then when it came to the second pass the thick edge was on the opposite side to that which it had occupied formerly. That was not always so, except in mills where one was under-de-winding on the pay-off side and under-winding on the reel side, or over-de-winding on the pay-off side and overwinding on the reel side. In that case, there had to be a turntable somewhere, which of course meant that the edges of the strip were reversed in position. Professor Ford was quite right in that respect. But where there was a big coil, it would

* Davy and United Engineering Co., Ltd., Sheffield.

be under-wound on the reel side and over-de-wound on the pay-off side. Where the coil was small, it could be over-wound on the reel side and the reverse on the other side, in which case rolling was carried on with the edge of the strip always on the same side of the roll.

Mr. Larke had shown some figures of mill production efficiency, which was a vital subject, and one to which Davy-United were giving a great deal of consideration. Although the designer should devote care and consideration to the design of the mill, that was not the only point which decided its operating efficiency. Among other important questions were: How efficient were the operators, not only individually but as a team? How good was the maintenance, both of the mill and of the ancillary equipment? How rapid was the team at their roll-changing drill? Was there a good supply of incoming coils to the ingoing side of the mill—a material on gauge and satisfactory in every respect—and could the finished product be got quickly away from the mill without hold-ups due to the handling equipment not being able to keep up with the mill.

Therefore, the problem was divided between the operator and the mill builder. The builders had developed mechanisms which almost automatically loaded the coils to the mills and took them away. Davy-United had recently set up an investigations section, part of whose task it was to go out and study mill production efficiency and suggest ways and means of improving it.

Mr. Larke had quoted figures which showed that for a certain mill run at 300 ft./min. the production efficiency was about 53%. He had gone on to show that doubling the coil length and doubling the mill speed did not yield the expected advantages. That was all very true. On the other hand, the modern five-stand tandem mill capable of speeds of 5000 ft./min. (for rolling tinplate), would give a production efficiency over a period of above 70%, and for short bursts could improve on that figure. What period had Mr. Larke covered when considering his results?

One way of improving production efficiency was by the employment of heavier passes, and of high mill speeds to cope with them. Full use must also be made of the available space. Another means to increase efficiency and cut down costs was to handle the pieces as few times as possible. On the modern non-reversing mills there was conveyor equipment for taking the coils back from the outgoing side to the ingoing side.

The problem must be surveyed from the point of view of both the large and the small producer. Obviously the small man had not got the production to warrant high-capital-cost mills. For the big manufacturer, the future trend would probably be along steel-mill lines, as had already happened in the case of aluminium. With the small number of alloys involved, producers got bigger runs and could use high speeds and steel-mill methods. In the United States aluminium industry, the hot line was similar to the modern semi-continuous hot-strip mill for steel rolling.

He thought the brass producers would follow the steel-makers in their own way, just as the aluminium producers had done. He would suggest, looking quite a long way into the future, that a high-production plant where most copper alloys could be hot rolled would take a form in which a two-high universal hot breaking-down mill dealt with a cake of 2000 lb. weight reducing to, say 3.75 in. and scalping to about 0.350 in. The strip would be brought to a three-stand tandem intermediate cold mill in flat lengths; it would be brought in on a sticker-type table, fed through the three stands, taking a 60 or 70% reduction, down to 0.12 in.; then sent straight off for annealing brought back—if necessary—and taken down to, say, 0.04 in. in one run through the three-stand. Further annealing would follow, and then in order to keep up with the plant, the strip would go to a couple of reversing small-work-roll mills. In the meantime, say, three or four coils would be welded

together, building them up into a 6000- or 8000-lb. coil. With such big coils one could employ high rolling speeds, and using a reversing set-up a great deal of conveyor equipment would be eliminated. For jobbing purposes, of course, coils could be taken off at any desired stage of reduction, and he thought it was important to maintain the maximum width of material as far as possible towards the finishing end.

If such a system was introduced, it would certainly cut down the cost of production, but the capital cost of the plant would be very high indeed compared with the type in use to-day.

With regard to the small man, Mr. Linford said that he did not think it possible to depart a great deal from the 1951 brass mill, a modern type of mill using all the advantages of a small work roll, good bearings, lubrication, and so forth. There would probably still have to be conveyor equipment.

MR. E. C. LARKE, referring to Mr. Linford's request for lost-time values, said that, roughly speaking, observations had been taken over a period of nine months. That included lost time when the mill was running. As regards the operator's efficiency, the information was based on a two years' analysis of time-and-motion study. One of the best incentives for increasing production was to pay the operator as much as possible and to introduce a piece-work system coupled with a co-operative effort, on his and the management's part to reduce lost time. A thousand reasons for lost time existed, but the engineers were by no means blameless. If presented with a really good analysis—drawn up on the same kind of basis as a time-and-motion study of the men's activities—of lost time due to engineering defects, he felt that a great deal could be put right from the maker's end.

To quote a few instances of points with which the engineer could deal, on most coilers there was an hydraulic pusher ram which simply pushed the coils off when finished. On practically every maker's plant he had seen the pusher gear prepare to ram the coil off the drum, stop because of inefficient operation of the hydraulic system, move back again, and make another attempt. This might happen three or four times before the coil was off the coiler. That sort of thing over a long period of time was very expensive from a production point of view. Again, when some part of the hydraulic system failed and it was necessary, for example, to undo a nut, one had to strip a complicated unit of the mill in order to get at that one simple nut to insert a bit of valve packing.

DR. A. R. E. SINGER,* B.Sc. (Member), said he had been particularly interested in the paper by Mr. Chisholm because it dealt with a subject to which far too little attention had been given. He wanted to say a few words about lubricants and cold rolling and the part played by friction.

Not very much was known about the coefficient of friction in rolling, or for that matter, in many other metal-working processes. Values for the coefficient were often used, but they were mostly overall values which happened to fit in fairly well with a rather simple analysis of what was going on during the rolling process, and a more penetrating analysis of the situation was very necessary to get some fundamental knowledge of what was taking place.

There were three principal methods by which the coefficient of friction could be determined. One of the simplest, and one that was used a very great deal, was not to worry about rolling mills at all but simply to squeeze two pieces of metal together and measure the force necessary for the movement of one over the other, and then to apply the results directly to rolling-mill practice. That method was open to very serious objections, and he would be opposed to the interpretation of such results in terms of rolling.

The second way was to take one accepted rolling theory, and after making

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some indirect observations on a rolling mill, to fit the various values of the observations to the theory and extract a value for the coefficient of friction. That was the manner in which values were often obtained but, again, a great deal depended upon the initial assumptions. If it was assumed, for instance, that the coefficient of friction was uniform over the arc of contact, then provided that that assumption was true, perhaps some reliance could be placed on the figure. But he did not think it was true; he thought it was a naive assumption. Undoubtedly the coefficient of friction varied a great deal over the arc of contact, and he would like to see some investigator try to find out just how it did vary. Some attempts had been made, but no very great success had attended them.

The third way was by using direct experimental methods. Again, one or two attempts had been made to do so, but the whole matter was beset by very serious experimental difficulties. Nevertheless, he felt that that was the way in which most progress would be made and the approach on which quite a lot of attention might profitably be concentrated, although admittedly little success had attended such efforts in the past.

It was apparent that the matter deserved serious study when the importance of the coefficient of friction was considered. It played a big part in determining the rolling load, the power consumption, and hence the heat generated; it helped to control the maximum draft that could be used; but even more important, it had a bearing on the actual load of deformation during rolling, and undoubtedly influenced the surface quality and surface condition of the strip or sheet produced by the rolling mill.

Mr. Chisholm did not seem to have mentioned the latter point in his paper, but it was one which concerned the producer a very great deal. If the overall value of the coefficient of friction was fairly high, burnished surfaces could be obtained in which a considerable degree of surface flow existed—polished or perhaps mirror-like surfaces. On the other hand, if certain good lubricants were used, a smooth matt finish resulted which was very desirable for other purposes. He would like to ask Mr. Chisholm if he could give any further information about the part played by lubricants in determining the surface condition of the strip leaving the mill, a matter which was so important to producers and users alike.

Mr. L. G. V. SKELTON* (Member) said that he did not think that Dr. Jevons had done justice to the value of X-rays in controlling the manufacture of these materials. This technique had been introduced into the laboratories of Richard Thomas and Baldwins a good many years ago, and they had been using it for more than five years almost as a substitute for the microscope, over which it had notable advantages. It was rapid and simple, it was non-destructive, and no sample preparation was necessary. It was very much quicker to put a sample on the X-ray set than to polish a micro-specimen, and almost untrained laboratory assistants could operate the modern X-ray equipment quite easily. The resulting photograph was a permanent record from which it was possible to assess the completeness of the annealing process, the grain-size of the material, and the degree of preferred orientation.

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CORRESPONDENCE

MR. L. S. EVANS,* B.Sc. (Member): On p. 467 of their paper Dr. Cook and Dr. Richards have explained why there is a limit to the degree to which metals can be cold worked. Many metals, e.g. copper, can be electrodeposited to give hardness values exceeding the maximum attainable by cold working, and it would be interesting to have the authors' opinions on this phenomenon.

In his discussion of materials for deep-drawing and pressing dies, Dr. Jevons (p. 580) mentions grey cast iron, and states that he does not think the graphite flakes contribute to the lubrication. It is true that the pressures are much higher than those present on the cylinder liner of an internal-combustion engine, but in the latter case it is known that the nature, size, and distribution of the graphite greatly affect the wearing properties; lamellar graphite is much superior in this respect to aggregate graphite, and other features of the micro-structure are also important. It may be that the same factors are operative in grey cast-iron drawing dies.

DR. E. W. FELL† (Member): As Dr. Jevons truly points out, the phenomenon of stretcher-strain markings is of scientific interest and of industrial significance. I would like to draw attention to some research of my own on this subject and concerned mainly with iron and steel. It included hardness tests,‡ X-ray-diffraction investigations,§ and a study of the influence of the direction of rolling of steel on the position of the markings.¶ A difficulty encountered in the work was in obtaining information regarding the presence of such markings in materials other than iron and steel. I am therefore particularly interested in Fig. 8 (a) (Plate LXV) of the paper by Dr. Jevons, showing stretcher-strain markings in aluminium-magnesium alloy sheet, because these are identical with the markings in steel.¶ A similar mode of deformation is thus indicated. I have measured the displacement associated with the formation of particular stretcher-strain markings.¶ Straight lines were inscribed on the polished surface of soft-steel bars. After loading the bars in tension to the correct amount, it was found that the lines remained straight in selected stretcher-strain markings of regular shape. This indicated simple shear. I described markings of the parallel-band type and the criss-cross-band type, shown in Fig. 8 (b) (Plate LXV), and similar yielding behaviour, in the case of Duralumin sheet strained by applied tension.§

MR. J. T. RICHARDS,¶ B.S. (Member): The following remarks are offered to supplement Dr. Jevons's extensive survey on press-working non-ferrous metals and alloys.

For the best results, it is generally advisable to draw or form the highest temper of beryllium copper strip that will withstand the fabricating operation. Solution-treated (annealed) strip should only be employed in the most severe operations, since it is not readily sheared in the die but tends to flow. In many cases, corrugated diaphragms are now being blanked and drawn from quarter- or half-hard strip with excellent results, whereas formerly solution-treated stock was almost always specified.

Table D gives an indication of the forming qualities of the several beryllium copper strip tempers before precipitation-hardening. A simple bend test

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‡ *Carnegie Schol. Mem., Iron Steel Inst.*, 1927, 16, 101.

§ *Ibid.*, 1937, 26, 123.

¶ *J. Iron Steel Inst.*, 1935, 132, 75p.

¶ Development Engineer, The Beryllium Corporation, Reading, Pa., U.S.A.

TABLE D.—*Minimum Radii for Forming 90° Bends in Beryllium Copper Strip.*

For heat-treatable material up to 0.040 in. thick.

Condition	Ratio, Punch Radius : Stock Thickness					
	Without Orange Peel Effect			Without Cracking		
	Angle with Rolling Direction, Degrees					
	0	45	90	0	45	90
Solution-treated .	0	0	0	0	0	0
Quarter-hard . .	0	0	0	0	0	0
Half-hard . . .	3.0	3.5	4.0	0	0	0
Hard	4.5	6.0	7.5	0	1.5	3.0

was used and the results are evaluated to two end points—minimum radius without producing “orange peel” effect and minimum radius without cracking.*

The rate of work-hardening beryllium copper is not substantially higher than that of other copper alloys. It merely appears higher as a result of the alloy's higher initial strength or modulus of plasticity. As shown in Table E, beryllium copper offers a higher level of tensile strength for a given degree of formability or ductility.

TABLE E.—*Relative Formability of Several Cold-Rolled Copper Alloys in Strip Form up to 0.040 in. Thick.*

Ratio, Punch Radius : Stock Thickness	Alloy	Temper †	Tensile Strength, lb./in. ²	Elongation, %
0 (sharp radius)	Beryllium Copper (2%)	0	63,000	52
	Brass (70 : 30)	0	47,000	62
	Phosphor Bronze (5%)	0	47,000	64
	Beryllium Copper (2%)	11	79,000	23
	Brass (70 : 30)	21	62,000	22
	Phosphor Bronze (5%)	21	63,000	28
4.0	Beryllium Copper (2%)	21	86,000	15
	Brass (70 : 30)	37	76,000	8
	Phosphor Bronze (5%)	37	80,000	10
7.5	Beryllium Copper (2%)	37	107,000	5
10.0	Brass (70 : 30)	60	95,000	3
	Phosphor Bronze (5%)	60	98,000	4

† Percentage reduction in thickness by cold rolling.

Table E compares the formability in all directions with respect to rolling or grain direction for beryllium copper, 70 : 30 brass, and phosphor bronze. The relatively high ratio for spring-temper brass and bronze is caused by the low formability of these alloys across the grain (90° to rolling direction). The higher strength level of beryllium copper, which generally limits commercial tempers to a 37% reduction of thickness (full-hard), prevents the occurrence of the marked directionality common in severely cold-rolled materials.

* J. T. Richards and E. M. Smith, *Proc. Amer. Soc. Test. Mat.*, 1950, 50, 1085.

MR. J. G. WISTREICH,* M.Sc. (Eng.), A.M.I.Mech.E. (*in further written discussion*): Messrs. Cleaver and Miller in Figs. 1 and 2 (pp. 541-2) of their excellent survey of wire-drawing practice have set out faithfully what the industry *believes* to be the best die shape for a given job, but it is becoming increasingly clear to those in possession of the B.I.S.R.A.† or other profilometers that what is believed to be the shape of a die seldom corresponds to the actual shape. In industrially shaped dies the reduction zone is generally curved and the average die-angle departs sometimes by more than 4° from that specified. Even greater discrepancies are encountered in the case of the parallel bearing; bearings either twice or half as long as specified are by no means unusual.

In these circumstances, and because measuring instruments of the kind referred to have become available only recently, I entertain serious doubts about the significance of the data in Figs. 1 and 2, and consider a thorough checking necessary before they are accepted. Needless to say even when optimum shapes have been defined, there still remains the formidable task of improving present-day grinding and polishing methods so that a specified shape can be made within fairly close tolerances.

In connection with die shapes, although the authors' argument about different optimum die-angles for different metals sounds convincing, it is apparently contradicted by Figs. 1 and 2. Why, for instance, should the die-angle for copper be 18° in diamond and 16° in tungsten carbide? The argument about the capacity of soft metals to transmit the work more easily suggests that the opposite should be the case.

Turning to the problem of die wear, I would add to the authors' list of causes (p. 548) one more—"die misalignment". As I have shown elsewhere ‡ misalignment between wire and die on the entry side leads to unsymmetrical wear, more frequent die changes, and shorter die life; misalignment on the exit side, practised deliberately in order to "cast" the wire, is often the cause of ovality, especially in dies with short parallel bearings or altogether without bearings.

I do not agree with the authors' diagnosis of the cause of ringing. A recent paper of mine § offers strong evidence that ringing is the outcome of the severe stress gradient close to the point of contact between the incoming wire and the die. The factors mentioned by the authors on p. 561 influence the rate of die wear generally and are responsible for wear ahead of the ring, but their effect on ringing is insignificant compared with that of the stress gradient. Further supporting evidence for my view is to be found in Cleaver and Miller's paper. I refer to their most interesting and valuable discovery that die rotation improves die performance and indeed suppresses ringing. I suggest that in rotating the die the authors so alter the system of stresses in the zone of deformation that the stress normal to the die is reduced, that lubrication is more effective and that—in as much as it concerns ringing—the stress gradient close to the point of contact between wire and die, is also reduced.

AUTHORS' REPLIES

DR. MAURICE COOK and DR. T. LL. RICHARDS: As Mr. Hessenberg implies, there are essentially three main approaches to the study of cold working of metals: electron theory, mathematical theory of plasticity, and structural examination. In view of the vast field to be covered, we decided to deal

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† R. M. J. Withers, *J. Iron Steel Inst.*, 1950, 164, 63.

‡ J. G. Wistreich, *Wire Ind.*, 1950, 17, 889.

§ J. G. Wistreich, *J. Iron Steel Inst.*, 1951, 167, 162.

almost exclusively with structure, as being most relevant to the subject of the symposium. Very few data were available, apart from those in the paper by Brick, Angier, and Martin, as to the possible connection between the electron: atom ratio of alloys and their deformation textures. The recent work of Dorn,* however, shows quite clearly that this ratio is of significance in determining work-hardening and indicates a profitable line of investigation of the plastic behaviour of metals.

With regard to the interesting contribution from Mr. Hentz, there can no longer be any doubt that crystallite formation plays a significant role in metal deformation. The fact that the crystallite size which he observed in deformed molybdenum is about a hundred times that estimated by Wood and Rachinger may, we agree, be associated with the higher temperature of deformation.

Mr. Wistreich will appreciate that, in what was a broad review, we were not able to deal in detail with surface textures, although these are of importance in certain instances, particularly bending. We agree that in a general sense it is change of shape which determines texture, and that there is perhaps more scope for a theory of the development of texture based upon flow than for one based upon any criterion of slip as in the recent paper by Calnan and Clews,† and previous papers by Taylor‡ and by Pickus and Mathewson.§

We are unable to agree with him, however, when he suggests that it is misleading to associate wire with tension textures. It may well be that the total load in tension in wire drawing may be considerably less than the total load in compression, but that the relative magnitudes of the corresponding stresses may be reversed, since these are defined by load per unit area of application.

Mr. Wistreich's observations on the structure and tensile properties of copper wire drawn with light and heavy drafts are interesting. Over the first stage of reduction, 30-40%, where deformation occurs by a slip mechanism, difference in magnitude of the individual drafts is, as one would expect, not accompanied by an alteration in mechanical properties (Fig. E). With greater reductions the difference in tensile strength for wire cold drawn by light and by heavy drafts can at least in part be explained, as Mr. Wistreich has shown, by the variation in surface texture. Since the direction of maximum Young's modulus and tensile strength for the copper crystal lattice is $\langle 111 \rangle$, then the inclination to the axis of the dominant $\langle 111 \rangle$ texture in the surface of wire drawn by light drafts accounts for its lower strength. Another factor that should not be overlooked is the possibility of there being greater residual stresses in the heavily drafted wire, since a series of small drafts may in some respects resemble a reeling process, which is often introduced not only to straighten a wire or rod but to redistribute internal stresses.

We are interested to learn that Professor Ford has observed that under certain conditions the onset of the shear mechanism of deformation in high-conductivity copper is sometimes delayed beyond reductions of 50%. In this connection it might be that, with the highly symmetrical system of stressing he employed, stable deformation textures are attained in which deformation can proceed to a more advanced degree by the primary slip mechanism. We agree with Professor Ford that the stresses in rolling are essentially compressional, but tensional stresses are undoubtedly involved, and Wever|| was the first to suggest that, for the purpose of rationalizing textures, rolling could be regarded as equivalent to deformation by compression normal to the strip surface and by tension in the rolling direction.

* J. E. Dorn, P. Pietrokowsky, and T. E. Tietz, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 933.

† E. A. Calnan and C. J. B. Clews, *loc. cit.*

‡ G. I. Taylor, *J. Inst. Metals*, 1938, **62**, 307.

§ M. R. Pickus and C. H. Mathewson, *J. Inst. Metals*, 1939, **64**, 237.

|| F. Wever, *Trans. Amer. Inst. Mech. Eng.*, 1931, **93**, 51.

With regard to the query raised by Mr. Evans on the hardness of electro-deposited metals, whilst the values realized may be associated with crystal structure, other factors are probably involved, and there would appear to be little evidence at present available relating the hardness of electrodeposits to that brought about by cold working.

MR. S. F. CHISHOLM: The use in my paper of vague and varied terms, as regards the part played by lubricants in the cold working of metals, is due to the fact that so little is known about the precise manner in which the lubricant functions. There appears to be some doubt about what is actually meant by "film strength" and "lubricity". These terms are rather loose, but I visualize a lubricant that has high film strength as one capable of preventing metal-to-metal contact, or able to prevent fusion of the strip and roll metals, or in simple language a lubricant that may be regarded as strong in compression. A lubricant said to have a high degree of lubricity is one that reduces friction, or in other words is weak in shear.

Professor Ford has understood the paper to state that the variation in viscosity of a lubricant with pressure is very small. If I have conveyed that impression, I should like to correct it, because a lubricant is very greatly affected by pressure. If the pressure between roll surfaces and strip is regarded as being of the order of several thousand lb./in.², the viscosity of the lubricant under those conditions of pressure is many hundred times greater than at normal atmospheric pressure.

This variation in viscosity with pressure is something that should not be regarded too lightly. It is known that petroleum lubricants differ quite appreciably in the extent to which they are affected by pressure. High-viscosity-index oils are not affected to anything like the same degree as low-viscosity-index oils. Although there is this wide variation in the effect that pressure has on the viscosity of mineral oil generally, it applies in a greater extent to fatty oils. That is probably the reason why fatty oils are so beneficial in many cold-working operations, quite apart from their greater ability to wet the metal surface.

Figures have been mentioned relating to the coefficient of friction of soluble oils, palm oil, and mineral oils. I do not think it safe to say that soluble oils have a certain coefficient of friction, because a soluble oil is a very complex mixture of various chemicals plus fatty materials in dispersion in water. Again, there is a wide variation in the types of soluble oils encountered.

Because oils vary so widely in viscosity with pressure, it is quite conceivable that a solid film exists between the strip and the roll surfaces. I agree with Professor Ford that it would be rather optimistic to believe that there is a hydrodynamic film between the strip and the roll surfaces, but the fact remains that, owing to the tremendous increase in viscosity, the lubricant is able to prevent pick-up or fusion, despite the fact that boundary conditions of lubrication prevail.

In regard to Mr. Davies's queries on intermediate rolling of brass, whilst it is suggested that higher-viscosity oils are more beneficial, the viscosity must obviously be controlled so that the reduction in friction is not so great that the rolls refuse to accept the strip. In this application the presence of lubricity additives would be a liability, but benefit can still be derived from the use of film-strength-increasing materials.

Another point raised is that even white spirit can be employed satisfactorily as a finishing rolling oil. That is quite true, but if a white spirit only is used, no great reductions can be expected, because it has a relatively low film strength. White spirits and materials of that nature, with a flash point of 110° or 120° F. (43° or 49° C.), may be quite satisfactory for the finishing pass on aluminium strip, if fed only by a drip feed on to the roll surface, but I

believe it to be extremely dangerous to use them in a circulation system as is necessitated by the present-day high-speed rolling. The spirit will be in a vaporized or atomized condition, so that one spark will set it alight. Despite the fact that it gives a very good finish on strip in its final pass, it is most unwise to use it on a flood basis.

In regard to Dr. Singer's query relating to strip finish, I agree that this is a most important consideration. Where friction is high, as is often the case when using low-viscosity rolling oils, a good surface finish is usually obtained, but where there is high friction, heavy reductions are not possible because of the liability to fusion of the strip and rolls, which would destroy the surface finish. By the use of higher-viscosity oils, friction is greatly lessened. This reduces the burnishing effect which results from the use of low-viscosity rolling oils, and normally produces a matt surface.

MR. C. E. DAVIES: I should first like to apologize for an error in Fig. 4 (p. 518). The lettering "Coiler drum" has been directed to the circles on each side of the mill that represent only the rollers over which the strip passes to the coiler drums, which are themselves not shown.

Mr. Hessenberg has referred to automatic control of strip gauge, and I shall be very interested to follow the progress made at Sheffield towards this desirable improvement. The trouble with a great deal of equipment of that type and also with load-measuring devices—I think every mill should be fitted with a reliable load-measuring instrument—is to obtain them in a practical commercial form. Many load-measuring devices are quite satisfactory from the scientific point of view, but it is not so easy to get a type that will stand up to rather rough usage in a mill.

Several speakers have dealt with pre-loaded mills. I am rather surprised by Mr. Hessenberg's statement that roll deformation may account for as much as 50% of the total yield of the mill. With a large mill the total stretch under load might be 50/1000ths of an inch. This involves not only extension of the housings, but also compression of the screws and bearings. It is true that such pre-loaded mills as have been developed do not take into account any deformation of the roll, and at the moment I do not see how this could be done. Developments in Sweden have been in connection with rod-rolling mills, and I believe a much greater degree of uniformity of gauge has been achieved by pre-stressing all the parts under load.

With regard to Mr. Fowler's comments on pre-loading, the housings are, of course, stressed to a much higher degree than in the ordinary rolling mill. A contact-type micrometer should control two of the major causes of gauge variation: changes in speed and non-uniformity of entry gauge. I think that Mr. Fowler is quite correct in his point with regard to the use of a cone-decoiler under back tension. The real difficulty is to find a means of obtaining a reasonable back tension on aluminium, which is so easily marked. The best solution seems to be the use of a bridle, the only alternative being a loaded press-wiper on the strip, which is more likely to cause scratching than any other equipment.

I am much interested in Mr. Fowler's experience that increased rolling speed results in improved production and general working efficiency. I have always felt that high speeds are desirable, especially for the softer metals, and in particular for aluminium. There are now mills rolling aluminium foil at 2000 ft./min., and the opinion of a practical roller who has hitherto not used speeds exceeding 100 ft./min. is that he can roll more easily at the higher speed; temperature control is simpler, and the tension applied by the coiler can be much lighter.

I am sorry to learn of Mr. Fowler's rather poor opinion of sheet rolling in four-high mills. Of course, it is unquestionable that sheet rolling in any

type of mill cannot compete with rolling in coils. The reductions have to be relatively light. The "billy-roll", to which reference has been made, has to my knowledge been very little used in this country. It was introduced to control the sheet as it enters the rolls so that a heavy reduction per pass may be taken. It has been proved in the case of hard steel, such as stainless steel, that the "billy-roll" does enable the mill, as the gauge becomes lighter, to take heavier reductions per pass.

Mr. Sims has referred to mill spring, automatic gauge control, and to roll eccentricity. The last is always a problem, because it is almost impossible to grind a perfectly concentric roll. I have been criticized for saying that back tension is unimportant. Perhaps it would be better to say that it is not so important as one might expect. Back tension and coiling tension will reduce the roll load, but mean wasting a certain amount of energy supplied by the coiler motor and absorbed by the brake or generator. The balance between the saving on the main mill motor and the expenditure of power on the auxiliary leaves a very small margin, and for many reasons I have always felt that there is no great point in having more tension in coiling than is necessary to keep the sheet flat.

There has been reference to the question of reversing mills against non-reversing mills. The time taken in adjusting screws is not very great in a reversing mill, but it involves re-setting for every pass, with possible change in gauge, and where otherwise suitable I think the batch rolling mill competes closely for productive output. With long coils there is much to be said for a reversing mill.

Within the scope of the paper, I could not deal with such details as screw-down gear, ejector gear, &c. The screw-down gear is very inefficient and uses a great deal of power to give very little result. It deserves study, and I feel that hydraulic loading might one day take its place, as it has on many light-gauge finishing mills.

On the question of cooling jackets versus sprays, cooling jackets keep the liquid controlled in a closed circuit, but they present many practical difficulties and less heat can be extracted from the roll than with an external spray.

Mr. Larke's comments on production and rolling efficiency are most interesting. I have seen a single-pass mill, dealing with small coils of non-ferrous metal, working with a rolling efficiency of about 95%. There was a very well-trained crew of two men, working on piece rates, and by the use of automatic coiling equipment the interval between each coil was so short that an even flow was maintained.

MR. F. T. CLEAVER and MR. H. J. MILLER: The contributors to the discussion who have referred to wire-drawing problems share a desire to obtain conditions of superior lubrication at the working dies. The methods suggested by Mr. Ashton are to some extent met by certain standard wire-drawing machines, in which the die mountings are water-cooled by internal circulation, and the wire and dies are provided with a high-grade lubricant. Such machines are frequently used for drawing steel wire, and may be more widely applied to non-ferrous metals in the future. For example, machines of this type have recently been used for drawing aluminium alloy wire, employing finishing speeds of 2500 ft./min.

Mr. Davies asked about the rotation of dies. At British Insulated Cables certain machines have been operated with a rotation of the last die at several hundred r.p.m. On these particular dies approximately twice the normal life has been obtained. This is an important result, and if confirmed on a larger scale, should lead to greater productivity owing to less time being wasted in changing dies, &c. This development is associated with improvement in lubricating conditions.

In America it is now fairly universal practice to produce rectangular-section copper wire, required in very large quantities for motor windings, in sections up to about $\frac{3}{4}$ in. wide and $\frac{1}{4}$ in. thick, by rolling in a tandem set-up, usually employing three horizontal rolls with two vertical rollers in between the three horizontal sets. Operating speeds range up to 1500 ft./min. The metal is flooded with a light lubricating oil, and the total reductions per pass through the tandem set-up are of the order of 50%, say 30–40% being effected in the first horizontal and vertical passes, 10–15% in the second passes, and a final adjustment only of the thickness dimensions in the last pass. It is obvious that very considerable heat is evolved with these reductions and speeds.

In this section-rolling technique automatic recording micrometers are used, a point that is of interest in connection with Mr. Hessenberg's doubt about the utility of such instruments. In this instance, when starting with coils about 2 tons in weight, the initial variation in dimensions of the drawn wire rod is not very great, and the mill operator has only to make three or four minor adjustments when rolling any one coil, these adjustments being made from the movements of the dial indicators which are graduated in ten-thousandths of an inch. However, it can be appreciated that if the ingoing metal has an irregular gauge, then the adjustment of settings with this type of micrometer may perhaps prove difficult. With the normal variation for this class of work, however, there is apparently very satisfactory gauge control.

Much interest attaches to Mr. Wistreich's remarks concerning the recent development of profilometers for determining die contours, and his finding that commercial dies sometimes depart very seriously from what might be termed the ideal shapes. We confirm his experience in this respect, but would like to differentiate between deviations that are accidental and those that are intentional. We think that some of the variations in question cannot be dismissed as accidental, although it must be conceded that in industry control of die shapes has not been as efficient as is desirable; certainly die shapes have not received the consideration inevitably devoted to finished wire dimensions.

The maintenance of wire-drawing dies to correct profile in the course of service in machines is not an easy matter, even with up-to-date equipment, and unfortunately die-reconditioning departments are not always equipped with the full complement of apparatus necessary for the essential control work. Even under good practical conditions, where the steel laps are accurately ground, there are unpredictable wear effects on the laps arising from (a) the condition of the abrasive, (b) the method of using the lap by different operators and in different machines, (c) the resistance of the stock to be removed. These all exert an influence in producing dies of varying shapes.

Apart from the accidental causes of variation, in many instances departure from the ideal shape may have been made because of reluctance to sacrifice die material when rectification becomes necessary. For instance, by shortening the length of the bearings from the recommended figures, dies can be employed for a further period at their approximate initial diameter instead of being opened out to much larger sizes. It is such considerations as these that could conceivably account for the wide diversity in practice to which Mr. Wistreich has drawn attention.

It is certainly worthwhile to make a further investigation of die shapes, and reconditioning practice, for the drawing of both non-ferrous metals and steel, and we look forward to any work that may be carried out on these aspects. The problem of arriving at the best possible compromise between initial design and maintenance, so as to reduce overall die costs to the minimum, resolves itself into an economic one, in which the following points have to be considered:

(1) Would the search for and maintenance of the optimum die shapes result in improved production life of dies, with either higher-quality wire or cheaper cost, or both?

(2) Would the accurate maintenance of die shapes add unduly to the overall costs?

(3) Can the correct profiles be consistently repeated in die departments by cheaper methods?

While we agree that misalignment of dies can be a variable factor, it is not as a general rule, a very important one. With most tandem and cone-type machines the position of the dies is governed by the design, and considerable wear of capstans is necessary to make an appreciable difference. Operating firms mostly maintain machines in such condition that the misalignment effect does not become too great.

We have noted Mr. Wistreich's recent paper concerning the contribution of the stress gradients to the phenomenon of ringing of dies. That vibration has an influence is demonstrated by the fact that in the drawing of copper wire there is little or no ringing effect at the first die, where vibration due to the brake-slip effect is nil, whereas it becomes increasingly noticeable from the second die onwards, where the vibration effects increase.

From the evidence available we think that the stress-gradient effect is of greater importance with steel than with the non-ferrous metals, and would instance two conflicting facts which it is necessary to reconcile. First, a much higher interfacial temperature is encountered when drawing steel, which would add to the stress gradient; secondly, using tungsten carbide dies, it is normal experience to obtain a longer working life with steel than with the non-ferrous metals, where the stress-gradient effect should be less. The vibration effects mentioned are only part of the story, and we believe that the cause of break-down of tungsten carbide dies in drawing non-ferrous metals is penetration of the metal into either surface cracks or cavities, so that the condition of "fouling" so commonly experienced in cold pressing and other cold-working operations, is set up. However, it may be quite wrong at this stage to make too stringent comparisons between copper- and steel-wire die practices until more recorded data are available.

DR. J. D. JEVONS: Replying to Mr. Hessenberg, it is difficult to make a general statement on the tolerances which users would like suppliers to work to, because so much depends upon the kind of forming operation to be inflicted on the sheet and also upon details of the tools used, particularly clearances. Quite often tolerances less than half those found in British Standard specifications are asked for, and regularly obtained, by users of non-ferrous sheet.

Mr. Polakowski's explanation of why the reverse method of re-drawing gives better results than the direct method will, I think, help to satisfy many who, like myself, have felt that the difference in the number and direction of the bends undergone by the sheet in the two methods would exert too small an influence to account for the very substantial difference in behaviour usually found in practice. The load/extension diagrams reproduced by Mr. Polakowski in Figs. H, I, and J suggest that the difference in the loss of ductility caused by the two different sequences of bending operations imposed during the direct and the reverse method of re-drawing is, after all, great enough to account for observed behaviour under the press.

Mr. Barlow questions my statement that, of the aluminium-magnesium alloys, the low-magnesium alloys behave best under the press. The instance which he gives to prove this will be of interest to many; nevertheless, I feel that, in general, my statement does represent industrial experience. An interesting detail to be seen in the results Mr. Barlow gives is the fallibility of the Erichsen test as a reliable guide to the behaviour of sheet under the press. Mr. Barlow's experience that with aluminium and its alloys a soft condition and a soft alloy are preferable for operations which involve "ironing", holds for most of the other industrial metals and alloys.

The stress/strain curves shown by Mr. Eborall, which reveal a clear relationship between the size of the initial "step" in the curve and the tendency of light-alloy sheet to develop either the "flamboyant" or the "parallel-band" type of stretcher-strain marking, are of very considerable importance.

The many references to observations of stretcher-strain markings given by Dr. Churchman will be welcomed by all who are studying this phenomenon. The suggestion that nitrogen may be of hitherto unsuspected importance in non-ferrous as well as in ferrous sheets will surprise many. May we hope that some work on this will be undertaken at Birmingham University?

Mr. Davis considers that a somewhat slower rate of crystal growth at annealing temperatures above 650° C. is likely to be the only advantage which a fine-grained 80 : 20 brass would have over a 70 : 30 brass for deep drawing. Mr. Egginton, on the other hand, confirms that the benefits I predicted for sheet of this kind are in fact experienced in industrial press-shops, and since the paper was published I have received confirmation of this from several other sources. It seems that wider recognition of the usefulness of the high-copper α -brasses in the press-shop is needed among both users and suppliers.

I am grateful to Professor Swift for his stimulating criticism. Answering his question concerning the usefulness of the tensile test in predicting behaviour under the press, I can assure Professor Swift that, when tensile tests form a regular part of the routine checking of sheet, by looking at the stress/strain curve of a piece of low-carbon steel or light-alloy sheet, men of experience can often form a remarkably accurate idea of how the sheet it represents will behave under certain press operations with which they are familiar. At present this test yields less useful information with brass, nickel silver, cupro-nickel, and copper, but this may be because in the industrial testing of these metals stress/strain curves are so seldom prepared that insufficient evidence at present exists for correlation with press-shop behaviour. The use of the tensile test for acceptance purposes is clearly difficult, because the shape of the stress/strain curve and the yield-point : maximum-stress ratio, two items not now specified, would be needed.

I am sorry that Professor Swift thought my criticisms of the wedge-draw test were directed at his investigators rather than, as I intended, at the test itself. Many workers have felt this test to be so promising that they have laboured, so far with little success, to overcome the side friction which seems to be the cause of the erratic results to which both Professor Swift and I allude. If this side friction could be minimized, it might well be that the wedge-draw test would give very informative results.

Regarding the somewhat controversial matter of the cup-drawing test, I agree that if this is to be used merely as a pass-or-fail test not more than two blanks of the same diameter need be machined from each batch of sheet. On the other hand if, as usually happens, one wants to know as much as possible about a sample and to be able to assess its deep-drawing properties, blanks of several diameters must be machined accurately to size and tested to enable the maximum diameter, as distinct from an arbitrary "pass" diameter, to be ascertained. I also agree that, to quote Professor Swift, his cup-drawing test has "gone at least some way to cope with the intrinsic complexities of the property known, but not yet understood, as drawability". No one questions the value of this cup-drawing apparatus in research, and we all hope that further development will make it more generally applicable as an industrial test. I myself think that at least three punch shapes (one circular and flat-ended, one circular and hemispherical-ended, and one rectangular and flat-ended) will have to be standardized. Attention may also have to be given to the method of blank-holding.

I apologize for having by inference included Professor Swift's own very valuable paper on lubrication in the general category of "vague and general". This is, of course, recognized as a notable exception.

JOINT DISCUSSION ON THE PAPERS BY DR. B. M. THALL AND PROFESSOR BRUCE CHALMERS: "MODIFICATION IN ALUMINIUM-SILICON ALLOYS"; AND BY DR. C. E. RANSLEY AND MR. H. NEUFELD: "THE SOLUBILITY RELATIONSHIPS IN THE ALUMINIUM-SODIUM AND ALUMINIUM-SILICON-SODIUM SYSTEMS."

(*J. Inst. Metals*, 1950, 77, 79, and this vol., p. 25.)

DR. C. E. RANSLEY *: In discussing the relation between the modification process and ternary-eutectic formation it is stated, on p. 45 of the paper, that: "The percentage of sodium required for full modification of the binary eutectic alloy corresponds very closely to that given above for the ternary eutectic composition" (i.e. 0.017% sodium). No evidence was cited for this statement, as it was thought to be generally recognized that a sodium content of about 0.02% was necessary for modification. The paper by Dr. Thall and Professor Chalmers, which appeared after our own had been submitted for publication, suggests however, that it may be worth while giving some experimental data.

Fig. A shows some results obtained by my colleague, Mr. L. Gwyther, on the relation between the sodium content and mechanical properties of a 12% silicon alloy allowed to revert by standing. The alloy was initially modified by the addition of 0.1% metallic sodium at 750° C. and the temperature adjusted to 700° C. A series of D.T.D. test-bars was then cast at intervals of 10 min., and corresponding samples were taken for analysis for sodium.

As sodium is lost by reaction at the melt surface, the U.T.S. and percentage elongation of the alloy first improve to a maximum value and then fall off again. The peak corresponds to full modification of the material, and it will be seen that this occurs with a sodium content of 0.017%, which is in exact agreement with the ternary composition. Other experiments have also given results very close to this value.

With an alloy containing about 8% silicon, the point of full modification occurs at about 0.10% sodium. As can be seen from Fig. 6 (Plate XIII) of the paper, the primary separation of aluminium from an alloy of this composition again leads directly to the ternary point.

Actually, the most finely dispersed 11-12% silicon alloy structures observed were those obtained in the solubility measurements, in which the alloy was soaked just above its liquidus temperature in contact with molten sodium and then cooled moderately quickly.

It is found necessary in commercial practice, in order to obtain uniform

* Remarks made in introducing his paper at the Annual General Meeting of the Institute held in London, March 1951.

modification, to make the metallic sodium addition at about 750° C. This is due to the fact that the ternary compound is formed immediately the sodium

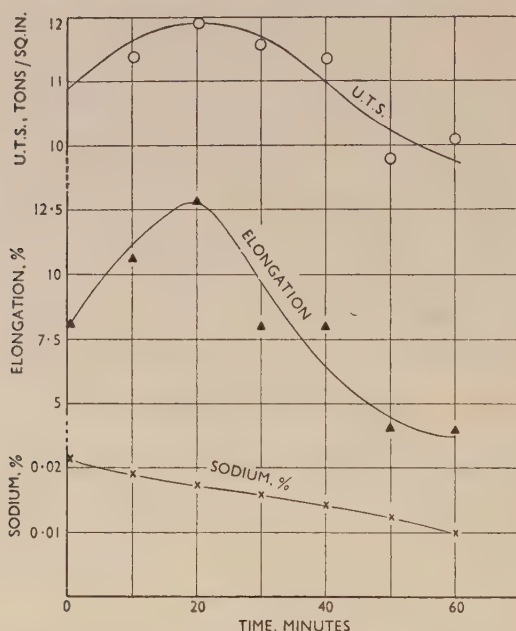


FIG. A.—Reversion of an Aluminium-12% Silicon Alloy on Standing, Showing Optimum Percentage of Sodium for Full Modification. (Ramsley.)

is plunged into the melt, and, being light, tends to float to the surface. A good superheat is necessary to bring the compound into solution before it reaches the top.

MR. E. H. BUCKNALL,* M.Sc., F.I.M.⁷ (Member): Dr. Thall and Professor Chalmers have produced an elegant explanation of how surface-tension effects, likely to be produced by modifying agents, may prevent the growth of a normal lamellar eutectic, interrupting growth of the minor constituent at a stage when it takes the form of short, stubby plates or spheroids, surrounded by the other phase. Nothing they say, however, indicates that the early formative stages of modified eutectics differ from those which apply to lamellar eutectic crystallization, and the reader may therefore be led to assume that the orientation relationships between the two phases in a modified eutectic are those which normally apply in lamellar eutectics. Nevertheless, the authors go on to suggest that their postulated mechanism may apply to spheroidal graphite in cast iron, of which the one outstanding feature is its spherulitic appearance with characteristic radial polycrystalline structure. The authors' observations on this apparent contradiction would be much appreciated and would undoubtedly be of great value in helping towards a full appreciation of the circumstances in which spheroidal graphite occurs in cast irons.

* Research Metallurgist, The Mond Nickel Co., Ltd., Birmingham.

DR. A. G. C. GWYER,* B.Sc. (Member): These papers have a special interest for me on account of the work which Mr. Phillips and I carried out † over 25 years ago on the modification of the aluminium-silicon alloys.

I am more particularly concerned with the claim of Dr. Thall and Professor Chalmers to have disproved our colloidal theory of modification. Their chief criticism appears to be based upon a misunderstanding, for they say on p. 84: "In order to account for the effect of sodium, the theory depends on the limited solubility of sodium in aluminium and silicon." This is quite incorrect. It is, of course, true that the solubility of sodium in these alloys is limited, but our theory is not concerned with this fact, and examples were given in our paper of the modification of other systems by the addition of elements that were completely soluble in the melts. We gave very fully our reasons for assuming that the modifying agent in the case of the aluminium-silicon alloys was not, in all probability, metallic sodium, but a compound of sodium, and we pointed out that with high percentages of added sodium, there was an additional constituent present. We were led to the conclusion that the modifying agent partook of the nature of a protective colloid, and we remain of the opinion that our colloidal theory offers a more satisfactory explanation of the mechanism of modification than any other yet advanced. The work of Ransley and Neufeld confirms the existence of the sodium-bearing compound referred to above, and it is also significant that they have adopted our theory as providing an adequate explanation of the general mechanism of modification.

In our paper, we included photographs showing the progressive effect of increasing additions of sodium upon the microstructure,‡ and Thall and Chalmers's radioactive experiments prove that, within limits, such additions do result in more and more sodium being retained in the alloys produced. Their results are, however, only semi-quantitative, and I fail to see what bearing they have upon their theory.

Finally, I must add that I find Thall and Chalmers's own theory of modification most unconvincing, as unless I have seriously misunderstood them, it seems to me to have no experimental basis whatever. In their own words, they assume "that a very small sodium content is able to reduce the interfacial tension between the solid aluminium and solid silicon phases" (p. 95), and then proceed to formulate their theory upon this assumption. So far as I am aware, there are no published values for the surface tensions at any of the possible interfaces, to say nothing of the effect of sodium upon them. If the authors have such evidence, they should certainly give it, as it is vital to their theory.

DR. H. K. HARDY,§ M.Sc., A.R.S.M., A.I.M. (Member): The theories of eutectic solidification mentioned by Thall and Chalmers were both put forward some time ago. || It is of interest to re-examine the problem in the light of the Volmer-Weber theory of rates of reaction based on Gibbs' equation for a critical nucleus size. ¶ This method of approach has been extended by several investigators and has recently been used as a basis for a general account of the mode of precipitation from solid solutions.**

* Lymm, nr. Warrington, Lanes.

† A. G. C. Gwyer and H. W. L. Phillips, *J. Inst. Metals*, 1926, 36, 283.

‡ Some of these are reproduced on Plate LXXV.

§ Head of Physical Metallurgy Section, Fulmer Research Institute, Stoke Poges, Bucks.

|| G. Tammann, "A Textbook of Metallography," p. 182. New York: 1925 (Chemical Catalog Co., Inc.).

R. Vogel, *Z. anorg. Chem.*, 1912, 76, 425.

¶ M. Volmer and A. Weber, *Z. physikal. Chem.*, 1926, 119, 277.

** H. K. Hardy, *J. Inst. Metals*, 1950, 77, 457.

The Crystallization of Eutectics.

The crystallization of a eutectic may occur at the equilibrium temperature, or below, where the common tangent to the free-energy curves of the solid phases passes below the free-energy curve of the liquid, as shown in Fig. B. The formation of the initial solid phase is governed by exactly the same conditions as those controlling the decomposition of supersaturated solid solutions by precipitation.* Embryos with the composition and structure of the solid are formed in the liquid and grow by unit processes until the stable nucleus size has been reached. These embryos possess a higher free energy

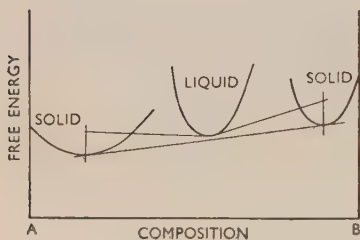


FIG. B.—Free Energy/Composition Curves for a Simple Binary Alloy Just Below the Eutectic Temperature. The lowest common tangent gives the composition of the stable phases. The free-energy drop per atom of the new phase is given by the vertical distance between the free energy corresponding to the composition of the solid and the tangent to the free-energy curve of the liquid at the composition from which the new phase is separating.* (Hardy.)

than the liquid owing to the energy of their interface, but, nevertheless, a "steady size" distribution of such embryos is to be expected. The minimum stable nucleus size is that at which further growth is accompanied by a reduction in free energy. The height of the energy barrier corresponding to this critical nucleus size depends on the free-energy drop per atom of the new phase and on the additional energy due to the formation of the interface. The solid phase formed initially from the melt will naturally be that with the greater probability of nucleation. Once the initial nucleus has been formed, subsequent solidification may follow either of the following processes:

(1) In which an easy-matching plane exists between the lattices of the two solids, so that the second phase is deposited on the initial nucleus. This will give rise to an orientation relation between the phases of the eutectic.

The first-formed nucleus, e.g. of composition *A* in Fig. B, grows rapidly until the concentration of component *B* in the immediately adjacent liquid has reached a value such that a plane of *B* atoms can be deposited on the matrix of solid *A*. The plane of *B* atoms grows until the concentration of *A* in the neighbouring liquids has been raised to a point where a plane of *A* atoms can be deposited on the solid *B*. The eutectic colony grows sideways by a continuation of this process as well as edgewise by diffusion and will possess simple orientation relationships derived from the original nucleus.

It may be noted that only a negligibly small activation energy is required for the deposition of the second phase on the original matrix. The energy barriers to this type of solidification process are shown in Fig. C (*a*), and there would be no undercooling other than that associated with the formation of the initial nucleus. This process is essentially similar to that accounting for the grain refinement of aluminium alloys.†

Similar considerations apply to a hypo-eutectic alloy in which the primary dendrites nucleate the formation of the eutectic structure. The copper-

* H. K. Hardy, *J. Inst. Metals*, 1950, **77**, 457.

† A. Cibula, *J. Inst. Metals*, 1949-50, **76**, 321.

phosphorus system appears to provide an excellent example, as the copper-rich dendrites are separated from the eutectic structure by a sheath of Cu_3P . Whether the final colony consists of parallel plates, as in the iron-carbon eutectoid, or of isolated particles depends on the relative quantities and growth rates of the two phases.

(2) In which no easy-matching plane exists between the two solids, so that the second phase is nucleated independently in the melt. There will then be no orientation relationship between the phases of the eutectic.

A layer of the second phase cannot be deposited on the lattice of the original nucleus under these conditions, and the energy barriers for this type of solidi-

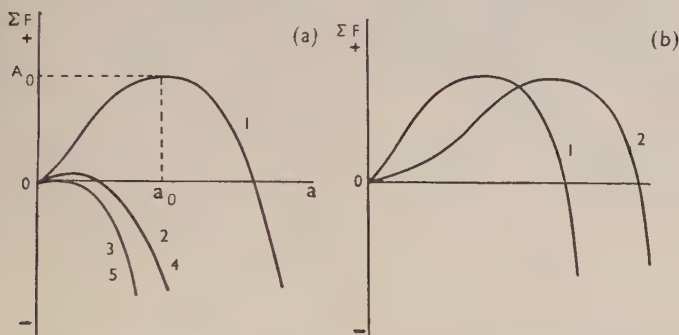


FIG. C.—Hypothetical Curves Showing the Variation with Size of Nucleus (a) of the Algebraic Sum (ΣF) of the Free-Energy Drop on the Formation of a New Phase and the Additional Interfacial Energy for the New Surface. A_0 is the activation energy required for the formation of a nucleus of minimum stable size, a_0 . (Hardy.)

(a) Eutectic solidification with an orientation relationship between the phases.

1. Formation of a nucleus of composition A from a melt of eutectic composition.
2. Deposition of a layer of B atoms on the lattice of solid A .
3. Deposition of a layer of A atoms on the lattice of solid B .
4. As 2.
5. As 3.

(b) Eutectic solidification with no orientation relationship between the phases.

1. Formation of a nucleus of solid A directly from the melt of eutectic composition.
2. Formation of a nucleus of solid B directly from the melt of eutectic composition.

fication process are shown in Fig. C (b). Nucleation will occur independently, but will be aided by the segregation due to the growth of the initial solid phase.

Typical eutectic structures and clearly defined eutectic colonies are not to be expected when the rate of nucleation is low, as both phases would have an opportunity to grow to relatively large particles. Typical eutectic structures will occur if the rate of nucleation is very high, as in supercooled alloys where a very large number of small particles will be formed.

Theories of Modification.

Thall and Chalmers have postulated that silicon particles are formed in the modified alloy at the normal eutectic temperature but that the presence of sodium causes them to be enveloped by the aluminium phase. The removal of these "seed particles" from contact with the liquid prevents their growth and causes undercooling to a temperature at which nucleation of silicon can occur very rapidly throughout the melt and thus give the very fine structure of the modified eutectic.

There is no easy-matching plane of good atomic fit in the aluminium and silicon lattices,* so that mechanism (1) above, by which silicon would be deposited on the aluminium, is not to be expected. Solidification would take place by the independent formation of nuclei of aluminium and silicon throughout the melt. A tacit requirement of the authors' theory is that the silicon particles formed in the modified alloy at the normal eutectic temperature shall be so close to the aluminium that they can readily be enveloped. This will be so only if the silicon particles arise in the liquid enriched in silicon immediately adjacent to the aluminium dendrites † and would occur equally easily at the normal eutectic temperature in both the modified and normal alloys. One must identify the particles of silicon formed under these conditions with the "seed crystals" of the authors, as there is no reason why nuclei inherent in the melt should be closely associated with the crystals of aluminium.

The seed crystals of silicon in the normal eutectic would be able to grow into the liquid and thus prevent undercooling. The primary crystals of aluminium have a marked dendritic habit, and it is difficult to visualize that these would have the ability to thicken perpendicular to their preferred direction of growth sufficiently rapidly to envelop every seed crystal of silicon in the modified alloy with complete success. Furthermore, the assumption of Thall and Chalmers that a reduction of surface energy between the solid phases would alter the angles between the particles of aluminium and silicon growing edgewise in their Fig 17 (p. 94) is not fully justified. The relative interfacial tensions determine the static equilibrium structure, but the angles in the growing colony are more effectively controlled by the relative rates of growth of the two phases, as the rate of cooling is never infinitely slow.

Ransley and Neufeld have suggested that the "protective colloid" theory of Gwyer and Phillips ‡ could be applied, since the ternary compound $[\text{NaAlSi}]$ could be formed on the surface of the initial particles of silicon and hinder their further growth. However, according to Ransley and Neufeld's paper, Fig. 15 (Plate XVI), the ternary compound can nucleate the formation of silicon particles, and its presence should therefore hardly hinder crystallization of the eutectic.

Thall and Chalmers investigated cooling rates of 15° – 90° C./min. Even with a cooling rate of 80° C./min. the normal alloy gave the ordinary eutectic value of 572° C. This strongly suggests that there may be some nuclei inherently present in the melt on which the silicon particles can grow at the normal eutectic temperature. Verö § has demonstrated that the number of primary silicon particles in a hypereutectic alloy is dependent on the thermal history of the melt. If sodium combined with these inherent particles, or markedly lowered their interfacial tension with the melt, a layer of sodium atoms would be adsorbed on their surface. This could well interfere with their ability to nucleate the silicon, so that the eutectic would not solidify until a lower temperature had been reached at which silicon particles could easily be nucleated directly from the melt. This would explain the lower solidification point of the modified eutectic on cooling and the constant melting point on heating. Although it requires the presence of inherent nuclei in the melt, it is not otherwise less attractive than the other theories

* L. K. Jetter and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1943, **152**, 166.

† It is assumed that the reduction in surface energy between solid aluminium and solid silicon is not so great that silicon can be deposited on the aluminium lattice. This assumption is quite reasonable, as this mechanism would prevent undercooling.

‡ A. G. C. Gwyer and H. W. L. Phillips, *J. Inst. Metals*, 1926, **36**, 283.

§ J. A. Verö, *Berg-u. hüttenmänn. Monatsh. Montan. Hochschule Leoben*, 1949, **94**, 301.

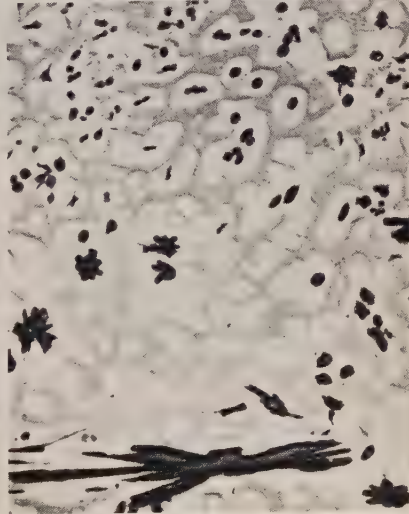
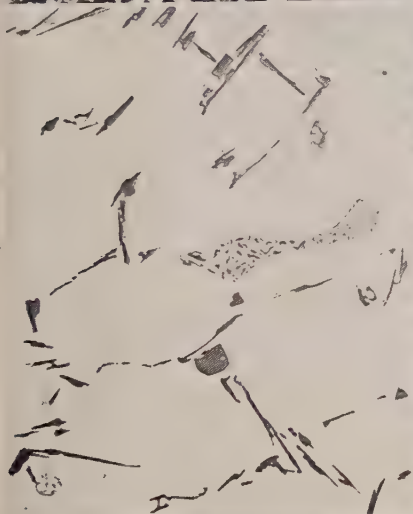
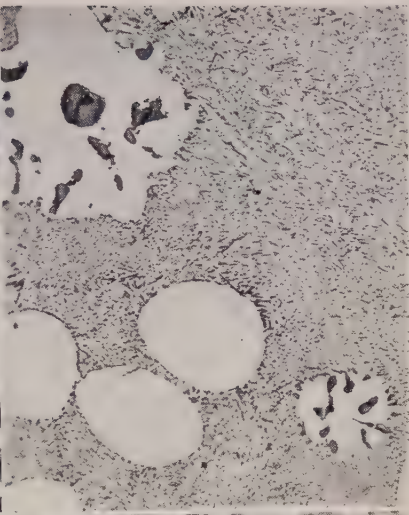


FIG. G.—Showing “Modification” in an Al-26.1% Cu-8.1% Mg Alloy; Furnace Cooled. On the right the quasi-binary eutectic Al-Al₂CuMg; on the left the ternary eutectic Al-Al₂CuMg-CuAl₂. Water etched. $\times 1000$. (*Mondolfo*.)

FIG. H.—Over-modified Al-12.1% Si-0.48% Fe Alloy; Sand Cast. Globules of AlNaSi₄ inside Al dendrites, probably as the quasi-binary eutectic Al-NaAlSi₄. Unetched. $\times 250$. (*Mondolfo*.)

FIG. J.—Under-modified Al-5.3% Si Alloy. Showing binary eutectic (coarse) and ternary eutectic (fine). Unetched. $\times 250$. (*Mondolfo*.)

FIG. K.—Binary Al-5.2% Fe Alloy; Chilled. Showing two primary phases and eutectic. Unetched. $\times 250$. (*Mondolfo*.)

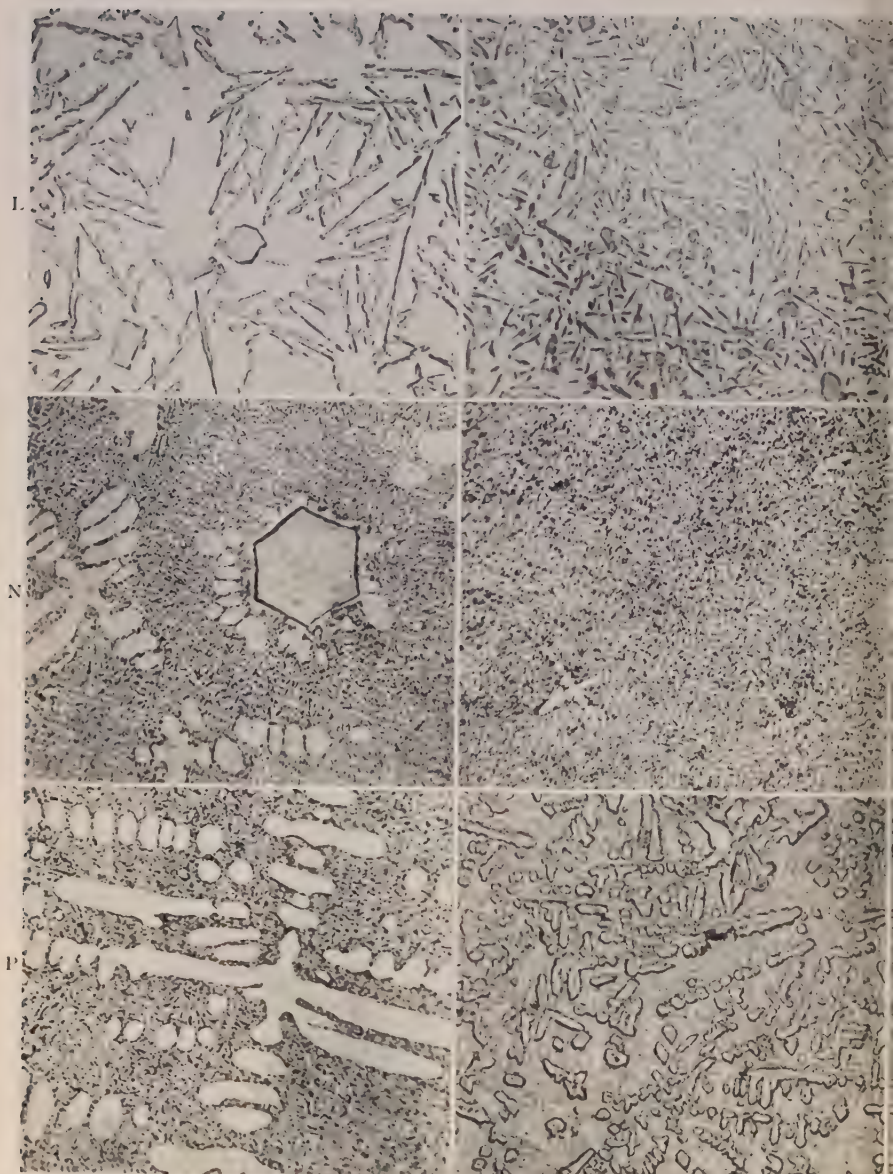


FIG. L.—Al 14.3% Si-0.35% Fe Alloy; Chill Cast, Fully Normal. Unetched. $\times 200$.
 FIG. M.—Same Alloy as Fig. L Treated with 0.01% Na at 750° C. Unetched. $\times 200$.
 FIG. N.—Same Alloy as Fig. L Treated with 0.05% Na at 750° C. Etched with HF. $\times 200$.
 FIG. O.—Same Alloy as Fig. L Treated with 0.10% Na at 750° C. Etched with HF. $\times 200$.
 FIG. P.—Same Alloy as Fig. L Treated with 0.20% Na at 750° C. Etched with HF. $\times 200$.
 FIG. Q.—Al 36%, Si 1.1%, Fe Alloy Treated with 1% Na at 1000° C.; Chill Cast. Unetched
 $\times 20$. (Gwyer and Phillips.)

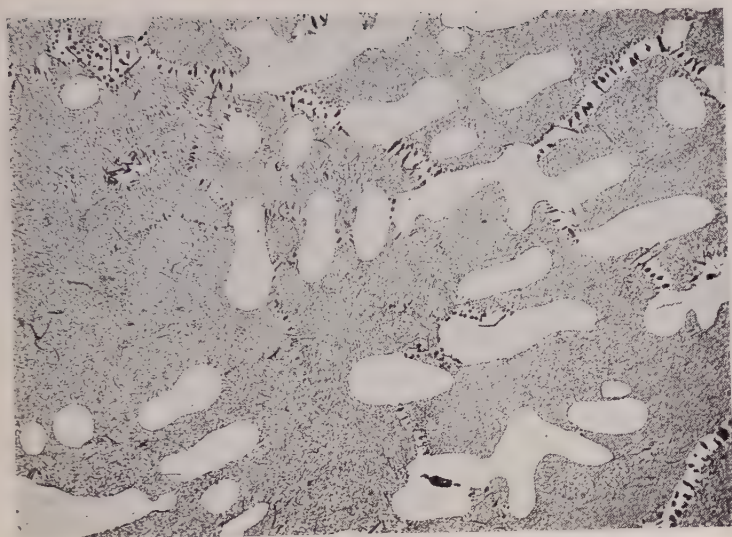


FIG. V.—Over-modified Al-Si Eutectic with Coarse Intercrystalline Bands.
 $\times 100$. (Scheuer.)



FIG. W.—Al-Si-Na Compound (NaAlSi_4) in (a) Unmodified and (b) Modified Structure. (a) $\times 200$; (b) $\times 400$. (Scheil and Zimmermann, cited by Scheuer.)

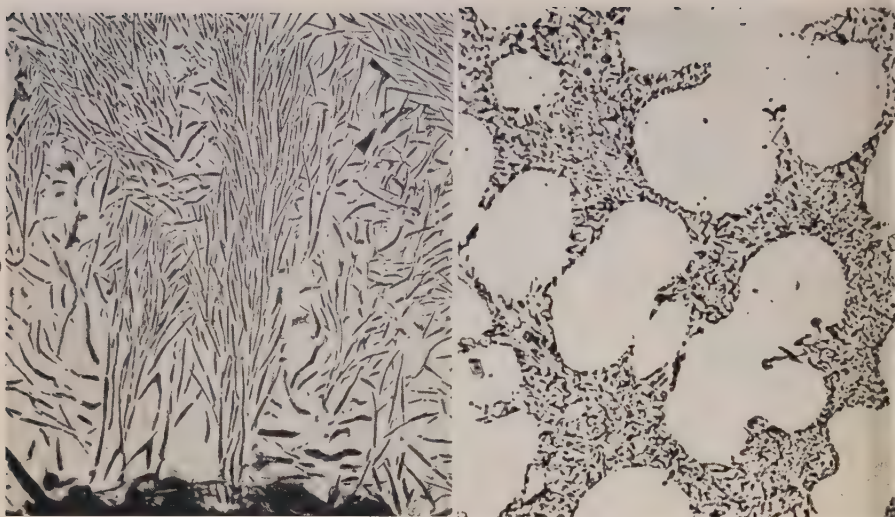


FIG. X.—Coarse (a) and Fine (Undercooled) (b) Fe-Graphite Eutectic. (a) Unetched. $\times 60$. (b) Unetched. $\times 150$. (Morrogh and Williams, cited by Scheuer.)

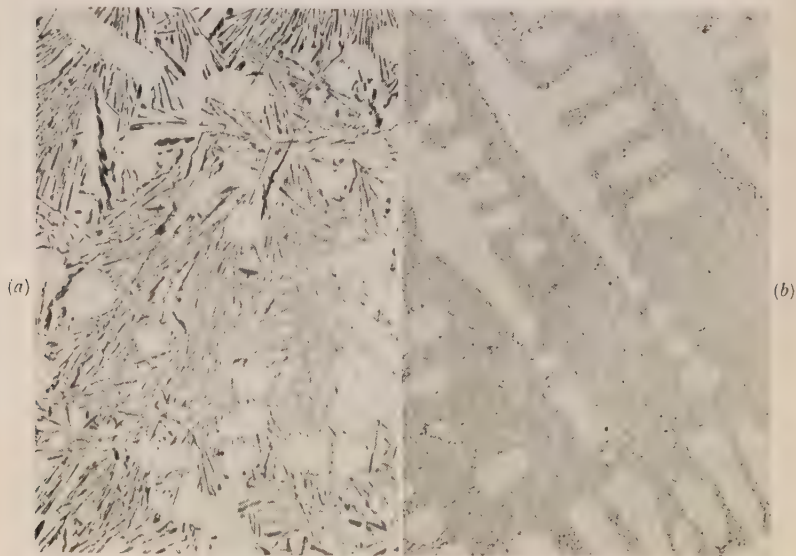


FIG. Y.—Unmodified (a) and Modified (b) Al-Si Eutectic. $\times 100$. (Scheuer.)

discussed above. It is worth pointing out that a satisfactory theory is still lacking to account for "over-modification".

DR.-ING. W. J. KROLL * (Member): Despite the fact that the modification of eutectic aluminium-silicon alloys with sodium or with sodium fluoride has been carried out for more than 25 years on a plant scale, no satisfactory explanation of the mechanism involved has been found. The interesting hypothesis advanced by Dr. Thall and Professor Chalmers should be examined in the light of some recent work which they have not mentioned. German investigations during 1939-45, led to the conclusion that the coarsening of sodium-free eutectic aluminium-silicon alloys is caused by the presence of very minute traces of phosphorus. Farnham and Potvin † report regarding this work that the critical phosphorus content is $0.00018 \pm 0.00005\%$. Hansen, ‡ referring to the same investigations, states that the phosphorus content must not exceed 0.00015%, since otherwise the silicon crystallizes in coarse grains. Photomicrographs confirm this statement, and mechanical tests show the following values for alloys with a given phosphorus content:

Phosphorus, %	Mechanical Properties
0.00054	Tensile strength, 23.0 kg./mm. ² Yield strength, 9.8 kg./mm. ² Elongation, 5.4%
0.00005	Tensile strength, 26.0 kg./mm. ² Yield strength, 11.9 kg./mm. ² Elongation, 8.4%

Sodium is said to neutralize the action of phosphorus, possibly by phosphide formation. This implies that stronger phosphide-forming agents would give better results than sodium, but calcium and magnesium, which presumably produce more exothermic phosphides than does sodium, do not function well as modifying agents.

The action of phosphorus, if confirmed, nullifies most of the theories on which modification by sodium has been based. It is hardly possible that as little as 0.001% phosphorus would have any effect in lowering the melting point of the eutectic and on the consequent undercooling. Such action should be attributable only to the sodium addition, when modifying with this reagent. However, surface-energy phenomena, as stressed by Dr. Thall and Professor Chalmers, might well be influenced by trace elements, such as phosphorus. A correlation of the effect of phosphorus and the action of sodium should be attempted in any future work concerning these alloys.

PROFESSOR L. F. MONDOLFO, § D.Eng. (Member): The theory proposed by Dr. Thall and Professor Chalmers is very interesting and provides an explanation of the modification of aluminium-silicon alloys which is in agreement with our present knowledge of the solidification process. However, I cannot see why they dismiss the ternary-eutectic theory as unable to account for the phenomena, since there are numerous facts in its favour. Moreover, the theory does not conflict basically with the explanation which they themselves give.

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† G. S. Farnham and R. Potvin, *Trans. Canad. Inst. Min. Met.*, 1946, **49**, 505 (in *Canad. Min. Met. Bull.*, 1946, (414)).

‡ M. Hansen, *et al.*, "F.I.A.T. Review of German Science, 1939-1946. Part I.—Non-Ferrous Metallurgy," pp. 16-17, and 128. Berlin: 1948 (Office of Military Government for Germany).

§ Illinois Institute of Technology, Chicago, Ill., U.S.A.

Work by Schulz * and by Nowotny and Scheil † indicates that a compound AlNaSi_4 is formed, which is probably an extension of the compound NaSi_2 in which some sodium is replaced by aluminium. The presence of this compound would make an equilibrium diagram of the type shown in Fig. D the most probable.

The zone of the diagram which concerns the modified alloys is similar to the corresponding zone in the aluminium-magnesium-silicon, aluminium-calcium-silicon, and probably the aluminium-lithium-silicon diagrams, and that explains the similarity of structures obtained. If, as is to be expected, no

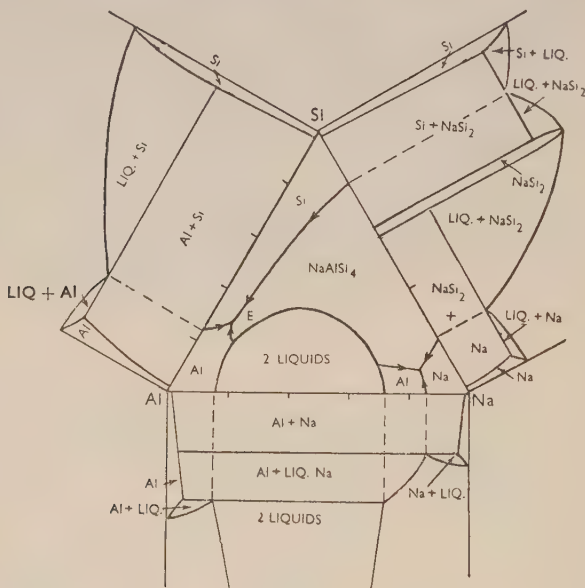


FIG. D.—Probable Form of the Al-Si-Na Equilibrium Diagram. Diagram not drawn to scale; important sections enlarged. (*Mondolfo*.)

ternary compound forms between aluminium, silicon, and lead (bismuth, cadmium), the resulting diagrams would be of the type shown in Fig. E, and no ternary eutectic would result at the aluminium end. Thus, lead, bismuth, cadmium, &c., cannot be expected to induce modification.

In Fig. D the ternary eutectic *E* would be the properly modified alloy. The fact that ternary eutectics exhibit a finer dispersion of phases than binary ones is well established, and a striking case is illustrated in Fig. G (Plate LXXIV). Over-modified alloys would show the presence of primary crystals of AlNa_2Si_4 or the quasi-binary eutectic AlNa_2Si_4 -Al, together with the ternary eutectic. Under-modified alloys would show the co-existence of the Al-Si eutectic (coarse) with the ternary (fine). Examples of these structures are given in Figs. H and J (Plate LXXIV).

The formation of a ternary eutectic results in a shift of composition from

* E. Schulz, *Z. Metallkunde*, 1948, **39**, 123.

† H. Nowotny and E. Scheil, *Metallforschung*, 1947, **2**, 76.

the binary and a lowering of the freezing point. Both are evident in the aluminium-silicon-sodium system. The fact that melting seems to occur at a

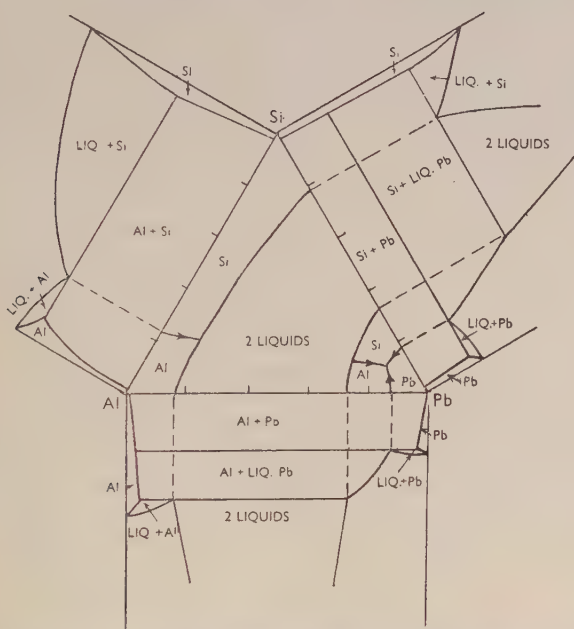


FIG. E.—Probable Form of Equilibrium Diagram of Al-Si-Pb(Bi, Cd) System. Diagram not drawn to scale; important sections enlarged. (Mondolfo.)

temperature higher than freezing is due to faulty experimental technique. Generally, in heating, the heat input is too high to obtain equilibrium. This is evidenced especially by the curve shown in the authors' Fig. 10 (p. 90), in which the melting actually takes place over a range of temperature. Another factor is the sensitivity of the measuring instrument. With an installation similar to that used by the authors, we have noticed that the Speedomax will read a slightly higher temperature when current is passing through the resistances of the furnace, than when the current is off. A good example of the effect of these factors is shown in Fig. F, which is a cooling and heating curve for high-purity aluminium.

Another feature very much in favour of the ternary-eutectic theory is the cooling curve reproduced by the authors in Fig. 12 (p. 91), which shows clearly the separation of the binary eutectic Al-Si, over a range of temperatures, followed by the constant-temperature freezing of the ternary eutectic. The



FIG. F.—Cooling and Heating Curve for High-Purity Aluminium. (Mondolfo.)

authors do not illustrate the microstructure of that alloy, but I should expect it to have patches of modified alloy together with non-modified.

The fact that modified alloys sometimes contain primary crystals both of silicon and aluminium does not conflict with the existence of a ternary eutectic; it only indicates local segregations, which are fairly common in non-equilibrium conditions. A good example of this is shown in Fig. K (Plate LXXIV). Once the existence of a ternary eutectic $\text{Al-NaAlSi}_4\text{-Si}$ is established, the refinement of structure is simply explained. When a binary eutectic solidifies, diffusion of one element in the liquid is sufficient to create conditions favourable for the growth of a phase. In a ternary eutectic two elements have to diffuse. Especially if one of these elements has a low rate of diffusion, the growth of the other phases is hindered and smaller crystals result.

MR. H. W. L. PHILLIPS,* M.A., F.I.M. (Member): May I draw the attention of Dr. Thall and Professor Chalmers to two or three points in their historical survey? At the top of p. 81 it is stated that the patent to Dr. Gwyer and myself covered modification by means of alkaline-earth metals, their oxides, and hydroxides. Actually, of the two patents quoted, one covers the oxides and hydroxides of the alkali metals, and the second the alkaline-earth metals and some other compounds of the alkali metals.

In discussing the theory advanced by Edwards and Archer,† that crystallization of the silicon is hindered mechanically by globules of sodium, the authors should, I think, have mentioned the alternative theory advanced, that sodium is adsorbed by the silicon crystals, thereby retarding their growth. This is of importance historically, as showing that as long ago as 1926 the idea was gaining ground, on both sides of the Atlantic, that surface reactions were involved in the process of modification, and that several investigators were beginning to think that the explanation would be found in some condition of transient stability.

The authors dismiss the colloid theory on the grounds that it requires the modified eutectic to be formed by the coalescence rather than by the growth of colloidal particles, and that it cannot account for the presence of two primary phases in the same ingot. In the paper by Dr. Gwyer and myself,‡ we did not postulate coalescence as essential: in fact, we stated that colloidal particles in general tended to grow or to coalesce, and that their rate of growth might be retarded by specific agents, the colloid protectors. I will deal later with the problem of the two primary phases, when I hope to be able to show that their presence is in no way inconsistent with the colloid theory.

It is most disappointing to find that, after devoting so much time and trouble to the development of tracer technique, Dr. Thall and Professor Chalmers were only able to report that sodium was actually present in the alloys to which it was added, and that the percentage depended on the amount added. This has been known for many years: Dr. Gayler was, I think, the first to demonstrate it by actual chemical analysis, 24 years ago, § and since the publication of Dr. Scheuer's papers, || the chemical estimation of sodium has become a matter of routine, permitting the loss of sodium on standing or remelting to be followed quantitatively. I am not sure that the authors are justified in drawing even these conclusions from their published figures. In Table II, alloy 2 (a 10% silicon alloy to which 0.1% sodium has been added)

* Metallurgist, Research Laboratories of The British Aluminium Co., Ltd., Gerrards Cross, Bucks.

† J. D. Edwards and R. S. Archer, *Chem. and Met. Eng.*, 1926, **31**, 504.

‡ A. G. C. Gwyer and H. W. L. Phillips, *J. Inst. Metals*, 1926, **36**, 283.

§ M. L. V. Gayler, *J. Inst. Metals*, 1927, **38**, 157.

|| E. Scheuer, *Z. Metallkunde*, 1933, **25**, 139, 157; 1935, **27**, 83.

gives 12,000 γ -counts/min. above background level, whereas alloy 6 (a similar alloy to which five times as much sodium was added) only gives 10,300 counts. The authors also claim that the percentage of sodium found depends on the rate of solidification. Surely it is the higher temperature attained after superheating, rather than the rate of solidification, that causes the greater loss of sodium.

I should be very interested to know if the authors attempted any experiments on autoradiography. Provided that the photographic emulsion had a sufficiently fine grain, it might be possible to use Na^{24} to determine what actually becomes of the sodium during modification. If it were found concentrated in an envelope round the silicon crystals, this would provide conclusive evidence in favour of the theories based on surface reactions. Whether such experiments could be carried out on these particular samples is perhaps open to question. They were irradiated after alloying and if, as I believe to be the case, Na^{24} can be produced by the irradiation of aluminium, the resultant activity might be distributed at random, thus vitiating the results. It would therefore possibly be better to irradiate sodium only, and use this for modification. I should be interested to hear the authors' views on this whole question.

Everyone will agree with the authors that some of the early thermal work will bear repetition, with the purer materials now available. But I doubt whether the use of a base-metal thermocouple and a high-speed recorder offers any advantage over the rare-metal couple and potentiometric equipment used by Dr. Gayler and by Dr. Gwyer and myself. Once again I have to record my disappointment that the results obtained add so little to our knowledge of the facts. The authors reached two conclusions: firstly, that the presence of sodium depresses the temperature of eutectic solidification, a fact that has been known for 25 years; and secondly, that the presence of sodium does not affect the liquidus temperature. The latter conclusion, which seems to have been based on two cooling curves only, is at variance with the extensive series of results reported by Dr. Gayler,* and also with our own, and in my opinion needs substantiation.

I suggest that the authors have not extracted the maximum possible information from their cooling curves. Surely an important feature of their Fig. 10 (p. 90) is the gradual, rather than the sudden, solidification of the eutectic, in line with the observations made by Dr. Gwyer and myself. Fig. R shows two of our original curves, for a normal and a modified 10% alloy, cooled at 8° C./min. The heating curve for the modified alloy is practically identical with the cooling curve for the normal alloy. On cooling, the modified eutectic begins to separate only a few degrees below the normal eutectic temperature, but even though silicon and aluminium nuclei exist, the crystals cannot grow rapidly enough for the latent-heat evolution to maintain a constant temperature. This feature is shown in Fig. 10 of the paper. It is difficult to make accurate measurements, but the inflection in the curve, indicating the start of the eutectic crystallization, seems to occur at about 570°, whilst the maximum heat evolution occurs at about 560° C. We found that similar cooling curves, with fully modified structures, could be obtained even with very slow rates of cooling, provided that all forms of mechanical disturbance were rigorously avoided.

It is an essential part of the authors' surface-tension theory that aluminium should be the leading phase during the eutectic separation, and that traces of sodium can reduce the surface tension between the solid aluminium and the solid silicon. The first assumption is not borne out by Dr. Gayler's 1927 work on undercooling, when she found that, on the outside of an ingot, silicon crystallized more rapidly than aluminium, whilst the reverse held for the

* M. L. V. Gayler, *J. Inst. Metals*, 1927, **38**, 157

central portion. A reduction in surface tension at the silicon/liquid interface is a necessary consequence of both the adsorption and colloid theories, and was indeed specifically mentioned by Dr. Gwyer and myself, so that the concept, that surface tension is a vital factor, is by no means novel.

Finally, I should be interested to hear the authors' explanation of the structures shown in Figs. L-Q (Plate LXXV), all taken from the paper by Dr. Gwyer and myself.

Fig. L (a 14.3% silicon alloy) exhibits the usual structure obtained in the absence of any modifying agent; silicon is primary. In the same alloy treated with 0.01% sodium (Fig. M) there is a general refinement, but no modification. If, as has been suggested, the normal eutectic is the binary one of silicon and aluminium, whereas the modified is the ternary eutectic of silicon,

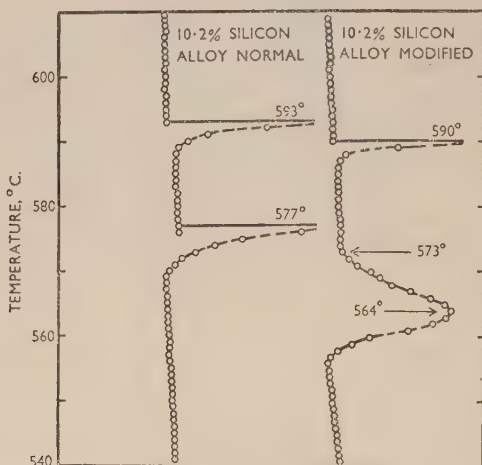


FIG. R.—Cooling Curves for Aluminium-10% Silicon Alloys, Normal and Modified, Cooled at 8° C./min. (Gwyer and Phillips.)

aluminium, and sodium, this alloy should, from Dr. Ransley's diagram, Fig. 6 (Plate XIII), show crystals of primary silicon, areas of coarse normal and areas of fine modified eutectic. In fact, its structure throughout is remarkably uniform.

The specimen treated with 0.05% sodium (Fig. N) shows two primary phases. There has not been enough colloid protector present to retard the growth of all the crystals, and exaggerated growth of some of the aluminium and silicon crystallites has resulted. As the composition lies on the silicon side of the eutectic point, it is possible that unprotected silicon crystals have grown to such an extent as to leave the melt supersaturated with respect to aluminium. Similar structures have been found in other partially protected colloid systems. With the alloy treated with 0.10% sodium (Fig. O) protection is at the optimum: the structure is fully modified, almost entirely eutectic, and the dispersion extremely fine. The 0.20% sodium structure (Fig. P) is over-modified, as shown by the eutectic coarsening. This coarsening is not due solely to retardation of cooling brought about by the primary separation of aluminium dendrites, as it can occur with an all-eutectic alloy. In our paper we attributed the coarsening to a change in surface tension caused by

excessive adsorption, but a possible explanation may be that colloidal protection is now so thorough that only a small proportion of the nuclei can grow, and that these give rise to larger crystals.

The alloy shown in Fig. Q, which contains 36% silicon, lies well on the silicon side of the eutectic, and modification with 1% sodium has thrown the primary silicon into a dendritic form. This change in crystal habit from the usual equiaxed or globular form must be associated with a change in surface tension, and here the tension involved must have been that between solid silicon and liquid. It cannot have been the tension between solid aluminium and solid silicon, which is the one held by Dr. Thall and Professor Chalmers to be involved in the modification process.

I suggest that the authors would have been well advised to limit this paper to an account of their work on the radioactive tracer technique. For this they are entitled to the fullest credit and priority, and it is their misfortune that it has yielded so little of value towards the solution of the problem of modification. The remainder of the paper contains few experimental results, and these, in my opinion, are inadequate to carry the theoretical superstructure.

MR. S. RAMAMURTHY,* B.Sc. (Member): Dr. Thall and Professor Chalmers have concluded that one of the main factors in the modification of aluminium-silicon alloys of eutectic composition by sodium, is the lowering by sodium of the interfacial tension between solid silicon and the melt.

The effect of the modifying agent, x , on the angle of contact can be diagrammatically represented as in Fig. S. If, as suggested, a similar mechanism

can be held to be operative in other alloy systems and there is a close analogy with the nodularization of cast iron, it becomes important to establish some criterion for the selection of a suitable surface-active, or modifying, agent in the case of any particular alloy. As shown in Table A, an interesting relationship is found to exist in four alloy systems between the atomic diameter of the basis metal, of the main alloying element, and of the modifying agent. In systems I-IV the atomic diameter of the modifying agent is in each case the greatest, the diameter of the main alloying element the smallest, with that of the basis metal falling between the two. In the lead-antimony system (V.) introduced in Table A for comparison, this rule does not hold good, and it has been shown by Thall and Chalmers that the improvement in the mechanical properties of the lead-antimony eutectic alloy brought about by a small addition of aluminium, is not due to modification. The atomic size-factor may, therefore, be to some extent significant in the choice of a modifying agent.

If modification is due to alterations in the interfacial relationships between the phases concerned, and if "size" is the governing factor, it is of interest to examine the relationship between surface tension and the size of the structural

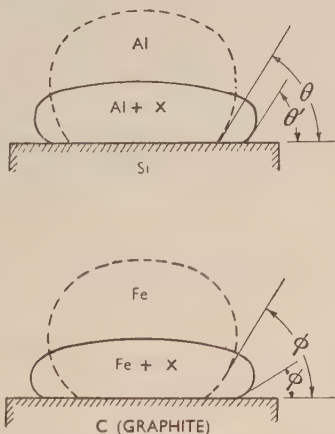


FIG. S.—Showing Influence of Modifying Agent on Angle of Contact.
(Ramamurthy.)

* Assistant Professor, College of Mining and Metallurgy, Hindu University, Benares, India.

TABLE A.—Relationship Between Atomic Diameters and Modification.

System	Element	At. Dia., Å.†	Remarks
I. Al-Si	Na *	3.83	Eutectic solidification temp. lowered by addition of Na (cf. Pb-Sb system).
	Ca *	3.93	
	Al	2.84	
	Si	2.65	
II. Fe-C	Ce *	3.6	Nodularization brings about a lowering of freezing temp. Ca added as its silicides exerts a strong influence on graphite size.
	Mg *	3.2	
	Ca *	3.93	
	Fe	2.52	
	C	1.54	
III. Ni-C	Ca *	3.93	
	Mg *	3.2	
	Ni	2.49	
	C	1.54	
IV. Co-C	Ca *	3.93	
	Mg *	3.2	
	Co	2.51	
	C	1.54	
V. Pb-Sb	Al *	2.84	Improvement in mechanical properties <i>not</i> due to modification. Eutectic solidification temp. <i>not</i> lowered by addition of Al.
	Pb	3.49	
	Sb	3.23	

* Modifying agent.

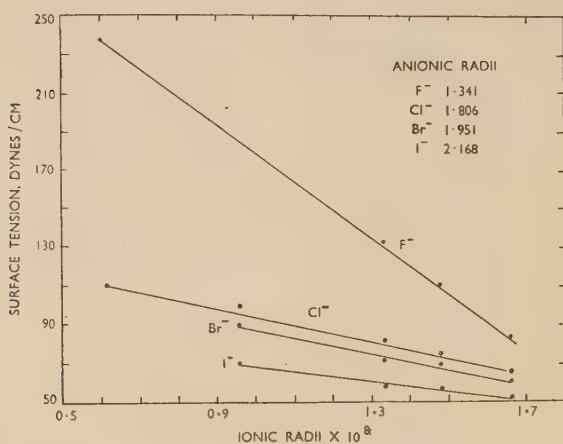
† Values taken from P. Duwez, *Metal Progress*, 1950, 57, 348.

FIG. T.—Radius of Cation against Surface Tension of Molten Halides at Constant Temperature (1000° C.) (Ramamurthy.)

units of a liquid. In Fig. T the surface tension of the molten halides of lithium, sodium, potassium, and caesium at 1000° C.* is plotted against their ionic radii.† It is worthy of note that an almost perfect straight-line relationship exists between these quantities. The order of the curves also follows that of the anionic radii of the halides.

DR. C. E. RANSLEY,‡ Ph.D., F.I.M. (Member): It seems to me that the theory put forward by Dr. Thall and Professor Chalmers leads to very considerable difficulties, and that the function of the sodium must, in fact, be to reduce the solid silicon/liquid interfacial tension and not the solid aluminium/solid silicon tension, as they suggest.

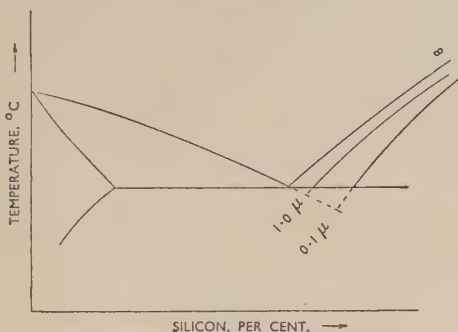


FIG. U.—Effect of Silicon-Particle Diameter. (Ransley.)
Values of r given against curves.

It should be pointed out that the solubility of a solid in a liquid is not an invariant quantity even at a fixed temperature, but is a function of particle size in accordance with the Thomson-Freundlich equation:

$$RT \log \frac{S_r}{S_\infty} = \frac{2\gamma M}{\delta r} \quad \dots \quad (1)$$

Here S_r is the solubility of particles of radius r , S_∞ that of particles of large radius (i.e. the "normal" solubility); M and δ are the molecular weight and density, respectively, of the solid phase, and γ its interfacial tension against the liquid.

If this equation is applied to the crystallization of silicon from molten aluminium at temperatures around 577° C., and a reasonable value is assumed for the silicon/liquid interfacial energy γ , say about 1000 dynes/cm., it will be seen that the effect of particle size starts to be appreciable at diameters less than 1 μ . At 0.1 μ dia. for example, the solubility of the silicon has increased from 11.7 to about 13.5%.

The equilibrium in the system can therefore be represented diagrammatically as indicated in Fig. U.

In the normal (unmodified) eutectic alloy, the aluminium, which does not undercool easily, probably separates first, and the liquid enriched in silicon

* Values taken from J. J. Bikerman, "Surface Chemistry for Industrial Research," p. 56. New York: 1947 (Academic Press, Inc.).

† Values taken from L. Pauling, "Nature of the Chemical Bond," p. 358. Ithaca, N.Y.: 1948 (Cornell University Press).

‡ Research Laboratories of The British Aluminum Co., Ltd., Gerrards Cross, Bucks.

will tend to precipitate it at a large number of centres. The particles formed, however, will be below the critical size at the temperature concerned, and will thus be unstable. They will therefore redissolve and eventually crystallization of the silicon will proceed on a relatively coarse scale from the small number of nuclei which reach a stable size, say $2-3\ \mu$. dia. During cooling at normal rates, equilibrium will thus be maintained at the S_{∞} value, i.e. at about 11.7% silicon.

Suppose now that conditions are such that the fine nuclei which are first formed do not redissolve, and that their growth is also hindered: the equilibrium will be shifted to the right in Fig. U, and the characteristics of modification will be produced. It will be seen that a reduction in the value of the interfacial tension γ in equation (1) leads automatically to an increased stability of particles of small radius and so can produce these effects. The ternary sodium compound is co-precipitated with the silicon and aluminium, and if it reduces the surface energy of the silicon will be adsorbed by it; it is significant that the amount of sodium present at the ternary point (0.017%) is just sufficient to form a monomolecular layer on 12% of silicon dispersed as $0.3-0.5\ \mu$ particles, and it seems probable that the various phenomena of modification can be explained on these lines.

DR. E. SCHEUER,* Dr.rer.nat. (Member): The diagram of the aluminium-sodium and aluminium-silicon-sodium systems produced by Dr. Ransley and Mr. Neufeld seem to be very convincing, and it is doubtful if anything new can be expected in future on this side.

Can Dr. Ransley from his observations confirm Scheil's † statement that the ternary compound does not form in all cases where the components are available in suitable concentrations? I have occasionally come across this compound in the practical handling of aluminium-silicon alloys without realizing its nature. For example, cases occurred where test-bars of aluminium-silicon alloys did not reach the tensile properties expected, despite suitable composition and complete success as regards the modification of the structure. The bars contained a constituent which was believed at the time to be a primary aluminium-silicon-iron compound, which owing to its plate-like form could be held responsible for the low elongation figures. However, no indication of an iron content which could explain the occurrence of primary crystals of this compound was obtainable from repeated and accurate analyses. Again, it is well known in aluminium foundries that a glittering fracture sometimes occurs in well-modified material, which according to its iron content should exhibit a fine, silk-like fracture. It seems probable that the presence of crystals of the ternary $[\text{NaAlSi}]$ compound is responsible for these puzzling fractures. Furthermore, the bands characterized by the occurrence of relatively coarse greyish crystals, which appear in over-modified alloys might now tentatively be interpreted as the ternary $\text{Al-Si-}[\text{NaAlSi}]$ eutectic (Fig. V, Plate LXXVI).

It would be most interesting to determine the conditions for the formation, or non-formation, of the ternary compound, so that its appearance could be safely suppressed without the necessity of keeping the sodium addition to the lower end of the range. Scheil † also observed the compound in unmodified structures (Fig. W, Plate LXXVI). Can Dr. Ransley confirm this observation?

The explanation of "sustained" undercooling advanced by Dr. Thall and Professor Chalmers, as due to the occlusion of silicon crystals by the growing aluminium phase is identical with that which I proposed in 1936.‡ It is now

* Chief Metallurgist and Head of Laboratories, International Alloys, Ltd., Aylesbury, Bucks.

† E. Scheil and R. Zimmermann, *Z. Metallkunde*, 1949, 40, 24.

‡ E. Scheuer, *Metal Ind.*, 1936, 49, 556.

supported by evidence and incorporated in a theory which accounts, in a simple way, for most of the important features of the modification process.

I do not agree with Dr. Ransley and Mr. Neufeld in attributing modification to the formation of protective films of $[\text{NaAlSi}]$. If such an effect existed, I should expect it to apply to both silicon and aluminium crystals; but in modified structures the aluminium crystals are notoriously large. Also, how would this theory account for the modifying influence of lithium? Moreover, as mentioned before, Scheil has shown that the compound occurs also in unmodified alloys.

With regard to the analogy between the aluminium-silicon-sodium system and the iron (nickel, cobalt)-carbon-magnesium (cerium) system, the originators of the nodular cast-iron process are inclined to assume that the fine iron-carbon eutectic known as "undercooled graphite" (as well as the nodular graphite) is not a true eutectic but a decomposition product of cementite formed immediately after solidification.*

A comparison of photomicrographs of the coarse and fine (undercooled) iron-graphite eutectic (Figs. X (a) and (b), Plate LXXVII) with those of unmodified and modified aluminium-silicon eutectic (Figs. Y (a) and (b), Plate LXXVII) reveals such a striking resemblance that it is hard to believe that the two pairs of structures should be produced by two entirely different processes.

In my opinion the cooling curves reproduced by Morrogh and Williams are not conclusive as regards the occurrence of undercooling; if it does occur, it is of the same "sustained" type as in aluminium-silicon alloys. Has the composition of the purely eutectic undercooled graphite been determined? It might emerge from such an investigation whether the structure is decomposed carbide (about 6.6% carbon) or eutectic (4.3% carbon).

None of the theories advanced account for the fact that all the agents—sodium, lithium, magnesium, cerium—which produce a fine structure are highly reactive. This might afford a new line of approach to the problem.

DR. THALL and PROFESSOR CHALMERS (*in reply*): We are very appreciative of the comments that have been made, particularly as it is apparent that the subject is by no means closed. We were not able to accept any of the theories previously proposed, for the reasons given in our paper. This view is apparently shared by Dr. Kroll and by Dr. Scheuer; we were not aware of Dr. Scheuer's proposal in 1936 of a theory similar to that under discussion. The most serious criticism of the new theory comes from Dr. Gwyer and Mr. Phillips, whose pioneer work in this field adds additional weight to their comments; but the "protective-colloid theory" seems to us to lack precision and to represent a description rather than a theory. Perhaps the theory under discussion, which essentially replaces the protective layer by a "Gibbs' adsorbed layer", may not be basically so different. It should be observed that, if a second phase is formed at low concentration, then the solubility must of necessity also be low. We not only admit, but claim, that the surface-tension effect is an assumption. It is well-established scientific method to attempt to explain diverse phenomena in terms of fewer hypotheses; when the attempt is successful, it is dignified by the title of a theory.

Regarding Mr. Phillips's comments on the second assumption, i.e. that one phase is ahead of the other in its advance into the liquid, it has since been shown that this is indeed the case for another eutectic system, that of lead and tin.† The reference to Dr. Gayler's 1927 paper in this connection is irrelevant, as we are not concerned with "speed of crystallization", a concept which in

* H. Morrogh and W. J. Williams, *J. Iron Steel Inst.*, 1947, 155, 321.

† W. C. Winegard, S. Majka, B. M. Thall, and B. Chalmers, *Canad. J. Chem.*, 1951, 29, 320.

any case should only be applied in circumstances which permit true dendritic freezing. It is incorrect to assume that our conclusions on melting and freezing temperatures were based on two curves only; numerous experiments were made under carefully controlled conditions, and the final view was reached as a result of critical examination of the evidence. It is nevertheless encouraging that Mr. Phillips points out that he and Dr. Gwyer had realized and referred to the importance of surface-tension relationships.

Autoradiographic determination of the distribution of sodium was considered, but it was decided that the resolution available with the present techniques was not sufficient for useful results to be obtained.

The remarks of Dr. Hardy and of Dr. Ransley are most interesting. We would suggest, however, in view of the recent work by Hollomon and his collaborators, that the effective nucleation process is probably heterogeneous, and not homogeneous as implied in the discussion.

Further consideration has led us to abandon the suggestion that the mechanism of formation of nodular cast iron is similar to the modification process.

Professor Mondolfo's comments on the ternary-eutectic theory are of much interest, but like the colloidal theory, this fails to account adequately for the formation of the modified structure under rapid cooling conditions in the absence of any modifying agent.

In conclusion, we would state that we make no claim to have solved all the problems relating to modification; our assumptions have not been fully substantiated by experimental evidence. Our hope is rather to have proposed a theory that at least is not at variance with the results of experiment, and our contention is that this cannot be said of any of the previous theories which were sufficiently specific to put to the test.

DR. RANSLEY and MR. NEUFELD (*in reply*): With reference to the points made by Dr. Scheuer, our experience tends to confirm the statement by Scheil that the ternary compound cannot always be detected in alloys containing enough sodium to bring them, under equilibrium conditions, into the primary field of the compound. We believe this is because it has a tendency to supercool very readily. Large plates of compound are only obtained at sodium contents a good deal higher than are likely to be obtained in normal modification in the foundry, unless, of course, the sodium is added at too low a temperature, so that it is not uniformly distributed in the melt. We have never found the compound to be present in unmodified structures, as reported by Scheil, and are unable to account for this particular observation.

The fact that sodium has no effect on the crystal size of the aluminium in modified aluminium-silicon alloys does not appear to us to have any significance as far as the adsorption theory of modification is concerned. The solid/liquid free-energy relations are probably very different in the two cases, and the adsorption forces on solid aluminium under these conditions may well be quite negligible in comparison with those on silicon. With regard to the modifying action of lithium, although the element itself is soluble in both liquid and solid aluminium, and in this respect differs considerably from sodium, it has recently been shown * that it also forms a ternary compound with silicon and aluminium with characteristics very similar to $[\text{NaAlSi}]$; it apparently has quite a limited solubility, so that there is no reason to suppose that the modifying action of lithium is any different from that of sodium.

* E. A. Boom, *Doklady Akad. Nauk S.S.S.R.*, 1949, **66**, 645.

DISCUSSION ON THE PAPER BY DR. T. M. CHANG AND: "SHEARING OF METAL BLANKS."

(*J. Inst. Metals*, this vol., p. 393.)

MR. J. F. HARRINGTON,* B.Sc., A.R.S.M., A.I.M. (Junior Member): Tests on blanking have been carried out at the Royal Mint, and the results are in close agreement with those of Professor Swift and Dr. Chang. It was also proved that the effect of a given tool shear is to reduce the maximum load by a definite amount, whatever the gauge. This is shown in Fig. A, where the maxi-

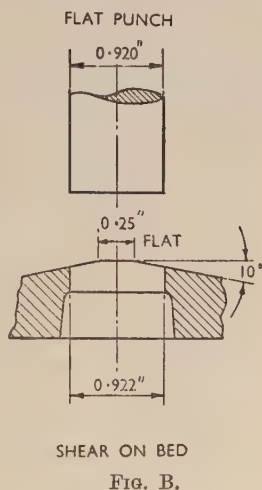
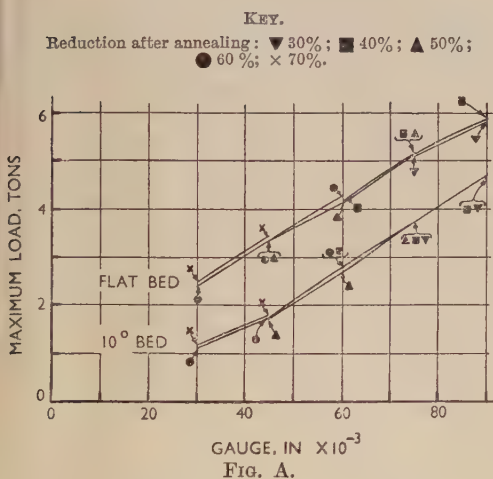


FIG. A.—The Effect of Tool Shear on the Maximum Load Required for Blanking Various Gauges of 75 : 25 Cupro-Nickel.

FIG. B.—Punch and Bed Used in Obtaining Results Marked "10° Bed" in Fig. A.

imum load required for blanking 75 : 25 cupro-nickel is plotted against the gauge. The tools used were of the same diameter and clearances. One curve gives the results using a flat punch and bed and the other those using the punch and bed made according to the diagram (Fig. B). The two curves are approximately parallel, and it is clear that the percentage reduction in maximum load obtainable by using shear is much greater with thinner than with thicker materials. With 75 : 25 cupro-nickel the percentage reduction given by rolling after annealing has little effect on the maximum load required for blanking. With 95½ : 3 : 1½ copper-tin-zinc bronze and 79 : 20 : 1 copper-zinc-nickel brass, however, the effect of the percentage reduction on the maximum load required was found by other experiments to be greater.

* Assistant to Production Engineer, The Royal Mint, London.

DISCUSSION ON THE PAPER BY MR. R. F. GILL, MR. E. A. SMITH, AND DR. R. H. HARRINGTON: "STRESS-AGEING TREATMENT AND ITS EFFECTS ON THE PHYSICAL PROPERTIES OF COPPER-, IRON-, AND ALUMINIUM-BASE ALLOYS."

(*J. Inst. Metals*, this vol., p. 203.)

DR. J. McKEOWN,* (Member): I have been very interested in this paper, but I cannot see that the authors have produced any evidence that stress-ageing differs from "strain-ageing". Their paper does not in fact mention the existence of the strain-ageing phenomenon, although its influence on the elastic and quasi-elastic properties of metals has been known for very many years. Thus, Muir showed the effect in a mild steel 50 years ago, while many investigators have demonstrated it in non-ferrous alloys.

I feel the authors have made a fundamental error at the very beginning of their paper when they state that at a stress corresponding to the room-temperature 0.2% offset yield strength (0.2% proof stress in England), no measurable or significant creep will occur at the ageing temperatures they used. I shall show later that for at least one of the materials employed this statement is by no means correct, and that the creep which does occur would be expected to have a significant effect on the properties resulting from the heat-treatment.

If an alloy is cold worked and then tested for elastic properties, it will be found that the stress/strain relationship is not linear or at least is linear only up to a relatively low stress. If this cold-worked material is then heat-treated below the recrystallization temperature, it will be found that a linear stress/strain relationship exists to a much higher stress than before the heat-treatment. This effect is referred to as strain-ageing.

Dr. O. F. Hudson and I † have shown that pure gold, silver, or copper will not strain-age, while dilute alloys of copper will do so. Thus, with high-purity oxygen-free copper we found that the limit of proportionality and the 0.01% proof stress were unaltered by low-temperature heat-treatments after 5 and 15% tensile overstrain. On the other hand, with tough-pitch copper containing 0.33% arsenic and 0.10% silver ‡ the limit of proportionality after 5% tensile overstrain was 1.2 tons/in.², and this was raised to 5.6 tons/in.² by a treatment of 2 hr. at 300° C. Again, a copper containing 1% tin and 0.02% silicon, and with 50% cold work, had its limit of proportionality raised from 4.0 to 20 tons/in.² by heat-treatment for 2 hr. at 300° C.

Strain-ageing is not found in the purest iron, but does occur if as little as 0.003% carbon is added. Thus, it appears that strain-ageing can occur only when some solute atoms are present.

I have always been attracted by the changes that can be brought about in the elastic properties of alloys by heat-treatment after cold work, and having

* Head of Mechanical Testing Section, British Non-Ferrous Metals Research Association, London.

† *J. Inst. Metals*, 1937, 60, 109.

‡ *J. Inst. Metals*, 1932, 48, 69.

available some 1% cadmium copper, I decided to test the relative effects of stress-ageing and strain-ageing. This copper contained Cd 1.03, O₂ 0.003 and P 0.014%, and had previously been given 20% cold work. It was annealed for 4 hr. at 500° C. and then cold rolled 64%. The results obtained are given in Table A.

TABLE A.—Effect of Heat-Treatments (Strain-Ageing and Stress-Ageing) on the Room-Temperature Tensile Properties of 1% Cadmium Copper, Cold Rolled to 64% Reduction.

Condition.	$E \times 10^6$, lb./in. ²	Limit of Proportionality, lb./in. ²	0.1% Proof Stress, lb./in. ²	0.2% Proof Stress, lb./in. ²	U.T.S., lb./in. ²	Elonga- tion, % on 2 in.	V.P.N.
As rolled	20.0 19.5	11,800 10,650	55,400 59,400	63,000 65,000	69,000 68,700	3.0 3.5	143
As rolled and aged 4 hr. at 175° C.	19.0 19.6	40,000 39,200	62,000 64,500	65,000 66,000	67,500 69,000	4.5 4.0	146
As rolled and aged 4 hr. at 225° C.	19.6 19.6	37,500 40,000	61,500 62,000	62,600 63,800	66,200 67,000	7.0 7.0	147
As rolled and stressed for 4 hr. at 175° C. at 58,500 lb./in. ² *	18.6	57,400	66,600	67,600	69,000	2.5†	...
As rolled and strained 0.13% plastic strain, followed by 4 hr. at 175° C.	19.0	43,800	65,500	66,300	68,000	2.5	...
As rolled, and strained 1.5% plastic strain, followed by 4 hr. at 175° C.	18.7	44,000	65,500	66,500	68,800	1.5	147
As rolled and stressed at 225° C. at 58,500 lb./in. ² *	Specimen broke in 3½ hr. at 225° C.					2.8	...
As rolled and strained 0.13% plastic strain, followed by 4 hr. at 225° C.	19.8	20,600	62,500	63,900	66,600	5.5	...
As rolled and stressed for 4 hr. at 225° C. at 46,200 lb./in. ² †	18.8	51,800	61,300	62,500	65,900	7.4§	...
As rolled and strained 0.06% plastic strain, followed by 4 hr. at 225° C.	19.3	50,600	63,500	64,700	67,000	8.0	...

* 58,500 lb./in.² corresponds to the 0.13% proof stress.

† 46,200 " " 0.06%

‡ This specimen extended 1.5% during the time it was stressed at 175° C.

§ This specimen extended 0.4% during the time it was stressed at 225° C.

No softening occurred at 225° C. over a period of 6 hr. It will be seen that strain-ageing at 175° or 225° C. produced a notable increase in the limit of proportionality and small increases in the 0.1% and 0.2% proof stress. The treatment at 225° C. reduced slightly the 0.2% proof stress. When a specimen was held for 4 hr. at 175° C. at the stress corresponding to the room-temperature 0.13% proof stress, and the room-temperature properties subsequently determined, the limit of proportionality and proof stresses had increased still

further. It should be pointed out, however, that during the time the specimen was stressed at 175° C. creep to the extent of 1.5% occurred, and this strain, in the direction of the axis of the specimen, may well have been responsible for the increase in the room-temperature properties. This possibility was not tested directly, but a specimen was overstrained 1.5% in tension and then aged for 4 hr. at 175° C. This treatment resulted in an increase in the values of the limit of proportionality and proof stress over those obtained by the ageing treatment alone. The limit of proportionality was not quite so high as that due to the stress-ageing treatment. The result, however, suggests that the direction of the working relative to the direction of the subsequent determination of elastic properties is important, i.e. tensile overstrain followed by ageing is more effective in raising the tensile elastic limit than cold rolling, where the straining is not completely in the direction of the axis of the test-piece.

The suggestion is made by the authors that stress-aged materials can be used as springs. This can surely not be based only on the improvement of elastic properties in one direction, for a spring has to withstand compressive as well as tensile stresses. Have the authors tested the elastic properties in compression and found an improvement? I suggest that they would not have found stress-ageing using tensile stresses to have produced any improvement in the compressive elastic properties.

On p. 209 it is suggested that stress-aged materials can be formed into springs after the stress-ageing treatment. Have the authors tested this? I have made a tentative reproduction of their proposal, but using strain-ageing instead of stress-ageing. A specimen of the 1% cadmium copper was strain-aged for 4 hr. at 225° C., after which it had a limit of proportionality of 45,000 lb./in.². It was then overstrained 0.344%, and when the limit of proportionality was redetermined it was found to be only 13,000 lb./in.². Thus, the working had destroyed the high limit of proportionality produced by the ageing treatment, putting the material back into the worked, unaged condition. I suggest, therefore, that stress-aged or strain-aged material cannot be formed into springs, if the forming operation involves plastic deformation, and still retain the requisite high limit of proportionality.

Finally, may I make a plea to those authors who quote limits of proportionality to state the sensitivity of strain measurement used in the determination of this property. In the determinations recorded in Table A a Lamb roller extensometer was used, the sensitivity of strain measurement being $\pm 2 \times 10^{-6}$.

MR. D. McLEAN,* B.Sc., (Member): This paper bears closely on some work by Mr. A. E. L. Tate and myself recently presented to the Société Française de Métallurgie.†

The authors' main conclusion is that, starting with cold-rolled material, the stress-ageing treatment raises the proof stress and—as judged by the electrical conductivity—increases the perfection of the crystal structure. Their explanation is centred around Fig. 3 (p. 212); they suggest that the observed effects are due to precipitation induced by local residual stress. This is a calculable effect, similar to the lowering of the freezing point of water by pressure, and its order of magnitude is indicated by the fact that to alter the freezing point of water by 1°C. a stress of about 1 ton/in.² is necessary. Now, the authors have found that stress-ageing works over a wide range of alloys, some containing more than one phase, some nominally single-phase. It seems unlikely that in all these materials, stresses of a few tons/in.² could produce sufficient precipitation to give the effects observed.

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† *Rev. Mét.*, 1951, 48, 765.

There is a different explanation, which should apparently be perfectly general and which seems more likely. For certain metals (aluminium, iron, zinc, magnesium) it is known from the work of Cahn* and others that the consecutive or combined action of strain or stress and temperature produces sub-crystallization, or polygonization; that is to say, the original crystals break down into a mass of sub-crystals. The sub-crystal boundaries are now considered to consist of rows of dislocations, since such an arrangement is one of lower energy than the more random arrangement characteristic of the cold-worked condition. As this criterion is independent of any particular metal, the polygonized condition is to be expected in all metals, although the unit sub-crystals may vary in size and might sometimes be so small as to be difficult to detect. The stress-ageing treatment of Gill, Smith, and Harrington must tend to produce this structure. The question is: Are the properties they find associated with this structure? I think there is enough evidence to suggest that the answer is "yes."

Because the rows of dislocations constitute an arrangement of minimum energy, a force is necessary to move a dislocation out of the row and thus cause plastic deformation. Ideally, this force would be much the same for each row. But in the cold-worked condition the dislocation binding varies over a range, and some dislocations will be relatively loosely bound. The dislocations are also loosely bound in the annealed condition. The loosely bound dislocations are anchored more tightly in the polygonized condition; consequently one might anticipate that polygonized material would possess a higher elastic limit and proof stress than annealed material or than cold-worked material containing a similar dislocation density. Moreover, as long as the polygonized condition persists, temperature should not affect this structural feature of few loosely bound dislocations, which should therefore also manifest itself in a higher resistance in creep; this possibility is suggested by the authors.

In our own experiments (*loc. cit.*) tests were made on annealed, polygonized, and cold-rolled super-pure aluminium. Annealed aluminium had a 0.1% proof stress of 0.25 ton/in.², and polygonized aluminium one of 3.1 tons/in.²; the effect of the polygonized condition is clearly in the anticipated direction. The cold-rolled material had a 0.1% proof stress of 4 tons/in.². However, it was cold rolled an arbitrary amount and almost certainly had a considerably higher dislocation density than the polygonized material; consequently the fact that it had a higher proof stress does not invalidate the foregoing argument. In creep tests at 200° C. under a load of 1 ton/in.² the approximate minimum creep rates were 1000%/100 hr. for the annealed, 0.17%/100 hr. for the polygonized, and 0.46%/100 hr. for the cold rolled condition. In this case the polygonized material is stronger than cold-worked material containing a considerably higher dislocation density.

The increase in electrical resistance produced by cold working is due to the scattering of electrons by the randomly placed dislocations. If the dislocations are concentrated into rows, the bulk of the metal consists of undistorted lattice and the resistance should decrease towards that of the fully annealed lattice, as the authors observe to occur as a result of stress-ageing.

The polygonized condition is therefore associated with those properties that the authors find to be developed by stress-ageing. I suggest that in some cases at least the reason why stress-ageing leads to the observed effects is because it produces, or tends to produce, a polygonized structure.

MR. J. T. RICHARDS,† B.S. (Member): In Table VIII (p. 208) of the paper the effects of stress-ageing treatments on the physical properties of copper-base

* *J. Inst. Metals*, 1949, **76**, 121.

† Development Engineer, The Beryllium Corporation, Reading, Pa., U.S.A.

spring materials are shown. Although beryllium copper is listed in the table, the effects of stress-ageing are not given. Were such tests conducted on beryllium copper?

The properties listed in the table for heat-treated beryllium copper are perhaps more convenient than typical. Cold-rolled or drawn beryllium copper strip, rod, or wire, even without heat-treatment, gives proportional-limit values in excess of 65,000 lb./in.², the figure quoted. For example, an average proportional limit of 74,300 lb./in.² resulted from approximately one hundred stress/strain curves for beryllium copper strip cold rolled 37%.* After precipitation-hardening, the proportional limit increases to around 150,000 lb./in.², values as high as 196,000 lb./in.² having been reported for strip.

Table B lists typical properties of beryllium copper wire, 0.057-0.080 in. dia., in various conditions. It should be pointed out that the average of elongation values for wire in the sizes given is generally considerably lower than those obtained from standard 0.250- or 0.505-in. tensile specimens. The values for beryllium copper from Table VIII of the paper are reproduced as Item 1 in Table B.

TABLE B.—*Typical Properties of Beryllium Copper Wire (1.8% Be) in Various Conditions.*

No.	Condition	Proportional Limit, lb./in. ²	Elongation, %	Electrical Conductivity, % †
1	Heat-treated (see Item 5, Table VIII).	65,000	1	21
2	Solution-treated, strained 35%	65,300	16	16
3	Drawn 37%	70,000	6	16
4	Drawn 50%	94,000	2	16
5	Drawn 76%	111,000	1	16
6	Solution-treated, heat-treated 2 hr. at 315° C.	120,000	9	22
7	Solution-treated, straightened, heat-treated 2 hr. at 315° C.	157,000	2	23
8	Drawn 50%, heat-treated 2 hr. at 315° C.	163,000	1	23
9	Drawn 50%, heat-treated 7 hr. at 345° C.	146,000	4	30
10	Drawn 50%, heat-treated 4 hr. at 370° C.	121,000	7	31
11	Drawn 83%, heat-treated 7 hr. at 370° C.	100,000	3	37

† International Annealed-Copper Standard.

An additional feature claimed by the authors is that stress-aged alloys have a much higher ductility than beryllium copper, so that they can be formed from stress-aged strip and wire, whereas beryllium copper must be formed in the solution-quenched condition and carefully precipitation-aged after forming. As a matter of interest, mill-hardened or pretempered beryllium copper (1.8% Be) strip and wire (not unlike tempered steel) have been available for a number of years. This product can be formed in the heat-treated condition and, at the same time, is free from the directional properties generally found in cold-worked brass or bronze products.

* J. T. Richards and E. M. Smith, *Proc. Amer. Soc. Test. Mat.*, 1950, 50, 1085.

Several special tests have been conducted to determine the influence of tensile overstrain and thermal treatment on beryllium copper wire. Test specimens were first strained well beyond the proportional limit by tensile loading, then stress-relieved for 2 hr. at 200° C. as a separate operation, and finally tested in tension to obtain the necessary stress/strain relationships. Time did not permit the establishment of the optimum stress-relieving operations, so that only the one treatment was considered. As shown in Table C, the results are similar to those that might be expected from "stress-ageing."

TABLE C.—*The Effect of Tensile Overstrain and Stress-Relieving on Tensile Properties of Beryllium Copper Wire (1.8% Be).*

Original Condition	Stress-Relieving Treatment			Proportional Limit, lb./in. ²	0.2% Offset, Yield Strength, lb./in. ²	Tensile Strength, lb./in. ²	Elongation, %
	Over-straining Stress, lb./in. ²	Time, hr.	Temp., °C.				
Solution-treated and straightened	none	52,900	64,900	91,500	22
	none	2	200	72,000	84,000	106,100*	12
	84,650	76,200	88,800	95,600	9
	84,650	2	200	88,200	96,000	112,600*	11
Drawn 50% and straightened	none	77,200	110,100	130,100	4
	none	2	200	102,000	127,700	134,600	2
	119,000	80,700	119,600	126,300	2
	119,000	2	200	104,000	135,000	137,200	2
Solution-treated, straightened and aged 2 hr. at 315° C.	none	150,900	200,000	206,800	2
	198,000	198,300	204,700	226,700	1
	198,000	2	200	203,200	206,700	208,500	1
Drawn 50%, straightened and aged 2 hr. at 315° C.	none	163,100	203,700	205,100	1
	200,000	167,800	210,100	212,800	1
	200,000	2	200	183,000	209,600	212,100	1

* Increase partially due to precipitation-hardening.

The authors would probably have obtained elongation values as low as those shown in Table B, if they had over-strained their specimens to the same degree.

The novelty of the stress-ageing treatment should be questioned in view of previously published work. In 1930 Macrae,[†] in presenting comprehensive data on overstraining at stress-relieving temperatures, obtained somewhat similar results. Research by various producers as early as 1935 led to the successful production of strand-hardened beryllium copper strip and wire. The resulting materials were found to offer higher strength (ultimate and elastic), ductility, and electrical conductivity than standard cold-worked and age-hardened products. In addition, by stressing the material at elevated temperatures it was possible to keep to straightness and flatness tolerances not otherwise attainable.

The role of precipitation in increasing elastic properties of stress-aged materials may well be considerably less than the authors contend, since the improved proportional limits can perhaps be explained more simply by the Bauschinger effect.[‡] Muir[§] and Macrae have shown that overstraining in tension, either coincident with or followed by suitable low-temperature

[†] A. E. Macrae, "Overstrain of Metals." London: 1930 (H.M. Stationery Office).

[‡] J. Bauschinger, *Zivilingenieur*, 1881, 27, 289.

[§] J. Muir, *Phil. Trans. Roy. Soc.*, 1900, [A], 193, 1.

treatment, causes an increase in tensile elastic values with a decrease in similar compressive characteristics. Precipitation, on the other hand, should yield higher elastic properties in both tension and compression and would probably cause a more marked increase in the ultimate tensile strength than that noted. Other investigators * have shown that overstrain or stress-relieving can cause appreciable improvement in the elastic characteristics of pure metals, such as copper or nickel, without the benefit of possible precipitation.

The changes in elongation and electrical conductivity attributed to stress-ageing can also result from suitable stress-relieving treatments.† For example, Moore and Beckinsale obtained a 100% increase in both proportional limit and elongation by stress-relieving 70 : 30 brass for 1 hr. at 275° C. The more marked increases in conductivity may in part be due to the precipitation of impurities or similar complex mechanisms.

The authors indicate that the most effective stresses for stress-ageing are those ranging from the proportional limit to the 0.2% yield strength of the alloy in its previously prepared condition. Galibourg,‡ however, has taken full advantage of the Bauschinger effect and by suitable overstraining and stress-relieving treatments has obtained for mild steels an elastic limit not only equal to the final ultimate strength but approximately 17% greater than the ultimate strength of the material in its original condition.

In considering the conservation of material possible through stress-ageing, the authors point out that present operational stresses may be borne by half of the present cross-sections. This may be true for the few applications calling for straight tension; however, in spring applications the possible reduction in cross-section is substantially less owing to the power relationship between stress and area. In the absence of evidence on the effect of stress-ageing on compressive and torsional properties, considerable care should be exercised before following the authors' recommendations on reducing cross-sectional areas.

* A. J. Phillips and A. A. Smith, Jr., *Proc. Amer. Soc. Test. Mat.*, 1936, **36**, 263.

C. S. Smith and R. W. Van Wagner, *Proc. Amer. Soc. Test. Mat.*, 1941, **41**, 825.

R. W. Mebs and D. J. McAdam, Jr., [*U.S.*] *Nat. Advis. Cttee. Aeronautics, Tech. Note No. 1100*, 1947.

† H. Moore and S. Beckinsale, *Trans. Faraday Soc.*, 1921, **17**, 162.

J. B. Kommers, *Bull. Univ. Wisconsin, Eng. Exper. Sta. Ser. No. 76*, 1933.

‡ J. Galibourg, *Compt. rend.*, 1932, **195**, 1022.

Editor's Note: No reply to this discussion had been received from the authors at the time of going to press.

DISCUSSION ON THE PAPER BY DR. T. P. HOAR AND MR. J. M. BUTLER: "INFLUENCE OF OXIDE ON THE PRESSING AND SINTERING OF COPPER COMPACTS."

(*J. Inst. Metals*, this vol., p. 351.)

MR. R. CHADWICK,* M.A., F.I.M. (Member): A low-density powder such as that used by the authors would be unsuitable for use in commercial compacting processes, for the large die fill-room necessary would lead to high tool costs, and automatic feeding would also be quite impossible. It is, however, typical of the raw powders produced by electrodeposition processes, and Fig. A (Plate LXXVIII) illustrates such a powder from another source the subsequent treatment of which may consist of light milling or barrelling, which causes the break up of the acicular and branching crystals that otherwise tend to interlock and impede movement between grains. Treated powders are of substantially increased packing density, but to obtain optimum free-flowing characteristics it is often necessary to remove some proportion of the fine particles.

The high densities and good flow properties that can be obtained in electrolytic copper powder can be seen by reference to a paper by Cook and Pugh.† Data from this and other unpublished sources are quoted in Table A, together with comparable figures given by Hoar and Butler. It will be noted that, in spite of differences in size-grading, density, and flow properties, all three powders give compacts of about the same density, which would seem to indicate

TABLE A.—Physical Characteristics and Compressibility of Electrolytic Copper Powders.

	Hoar and Butler Untreated Powder	Treated Powders	
		Fine grade	Coarse grade
Percentage passing 240 mesh . . .	67	65	20
Apparent density, g./c.c.	1.27	1.59	1.88
Tap density, g./c.c.	1.68	2.56	2.63
Flow: $\frac{3}{16}$ in. dia. orifice	Nil	Nil	Good
Density of compact made under pressure of 20 tons/in. ² , g./c.c. . .	7.0	6.8	7.2

that the powders were all reduced to the same physical condition by fragmentation in the die during the compaction process. Probably, therefore, the compacts made by Hoar and Butler were much closer in structure to those made from treated copper powders referred to by Cook and Pugh than might be supposed from the physical characteristics of the powder used.

* Assistant Research Manager, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

† *Iron Steel Inst. Symposium on Powder Metallurgy, Special Rep. No. 38, 1947, 162.*

The method of pressing powders in a completely unlubricated parallel-walled die is one likely to result in very high wall friction, especially in such a small-diameter product, and this may give rise to erroneous estimates of the pressures applied to the compacts. In view of the difficulty commonly experienced in pressing under such conditions, it is indeed surprising that the authors have obtained such consistent results, and it seems possible that the cleaning operation provided some measure of lubrication. Fig. B shows the

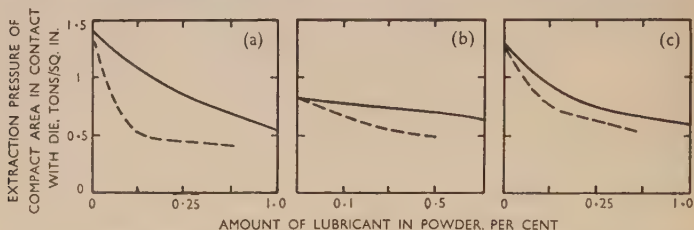


FIG. B.—Die-Wall Friction for Copper Powder Compacts Pressed at 25 tons/in.² in Parallel-Walled Dies: (a) Steel; (b) Chromium-Plated; (c) Porcelain. (Chadwick.)

—— Using graphite lubricant.

----- Using zinc stearate lubricant.

effect on die-wall friction of lubricant incorporated in the copper powder using data derived from measurements of the load required for extraction. It will be noted that very small percentages of either zinc stearate or graphite substantially reduce the frictional load, and that as the proportion of either lubricant is increased the load tends to the same low value for all three die materials. There are obvious objections to the use of these internal lubricants when the sintering process is being investigated, but equally good lubrication can be obtained by light smearing of the die walls between each pressing operation, although such a procedure is less convenient in automatic pressing

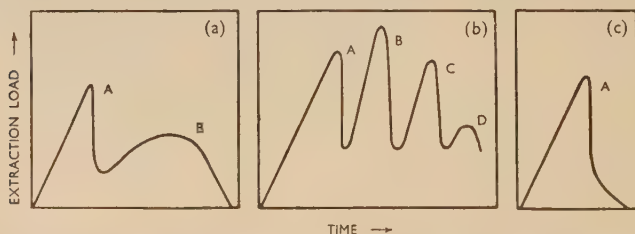


FIG. C.—Die-Wall Friction During Ejection of Copper Powder Compacts from (a) Lubricated Parallel-Walled Die; (b) Parallel-Walled Die without Lubricant; (c) Tapered Die.

operations than the incorporation of lubricant in the powder. In the complete absence of lubricant, however, a very considerable advantage is derived from the use of a chromium-plated die.

In the pressing of copper powders without lubricant, both pressing and ejection operations tend to proceed in jerks. Typical load measurements which illustrate this for the ejection stroke are reproduced in Fig. C. Before ejection begins the load builds up to a value A, depending upon the state of lubrication of the die, whereupon there is a sudden release of load accompanied by movement of the compact. If lubricant is present, the load may

again rise to a second, lower, peak *B*, and finally fall away to a small value. Without lubricant, however, there will generally be a series of peak loads, *B*, *C*, *D*, &c., which cause chatter, and may also result in mechanical damage to the compact, associated particularly with the sudden changes in compressional stress at the die mouth as the compact emerges. Ideal conditions are realized only with a tapered die, where the first movement of the compact at *A* is followed by a rapid fall of ejection load to zero.

The authors' deductions with regard to the probable mechanism involved in sintering, and the associated structural changes, appear to give a very complete explanation of observed dimensional changes, but they would have been very much more satisfying and acceptable if they had been accompanied by micrographic details of the structures obtained at the various stages of sintering. However, the suggestions made regarding the changes taking place below about 400° C., when the compact is still in a more or less unsintered condition, appear to be reasonably acceptable, and confirmation by more direct observations would be difficult, since no real structural changes are involved.

In considering the expansion of compacts that occurs at higher temperatures, Hoar and Butler put forward a complex theory (p. 370) regarding the reduction of the oxide film surrounding the individual copper particles, and the formation of a continuous copper film superimposed on the oxide layer. According to Table III (*a*) (p. 375) most of the oxygen is removed at 435° C., while reference to the paper by Cook and Pugh shows that a considerable measure of recrystallization occurs in a copper powder compact after heating for only 10 min. at 400° C. In the light of these two facts it is difficult to understand just where these copper films are formed, and in the absence of concrete micrographic evidence the theory put forward cannot readily be accepted. Bearing in mind, however, that the compacts are probably recrystallized during thermal treatment at temperatures between 400° and 950° C., it would be more reasonable to assume that conventional gassing is involved. In support of this it may be noted that by gassing tough pitch copper with hydrogen at 800° C., a volume expansion of about 8% is obtained, so that the mean linear expansion is of the same order as that observed by Hoar and Butler.

In referring to the mechanism of gaseous diffusion in a compact the authors suggest that, depending on the amount of compaction and degree of sintering, certain pores will be open to direct gaseous diffusion while others will be sealed. However, for any given type and grade of powder, there is a definite density of compaction at which permeability to gases ceases quite sharply. The relationships between porosity, permeability, and compaction pressure for iron powders containing graphite have already been reported.* For copper powder of the type used in the present experiments, the critical porosity would probably be about 18%. According to Table II (p. 359), therefore, the 0.11% oxygen powder would be permeable when pressed at 20 tons/in.², but impermeable when pressed at 30 tons/in.², while the 0.20% oxygen powder would become impermeable under a pressure of just about 30 tons/in.². All powders of higher oxygen content, being less compressible, would be readily permeable over the whole range of pressures investigated. This would account for the expansions observed in the 0.11 and 0.20% powders, indicated in Fig. 15, without the complicated explanation involving a sealing action at some stage in the sintering operation put forward on p. 373.

DR. W. D. JONES,† M.ENG., F.I.M. (Member): It has always been realized that the oxygen content of metal powders is a very important matter and its pre-

* R. Chadwick and E. R. Bradfield, *Iron Steel Inst. Symposium on Powder Metallurgy, Special Rep. No. 38, 1947, 123.*

† Director, Powder Metallurgy, Ltd., London.

sence generally regarded as highly deleterious. The authors show, however, that this may not necessarily be the case and in fact that there may be an optimum percentage of oxide for the maintenance of the most desirable sintering conditions. For example, they show that with varying percentages of oxide the final sintered density may be unaltered, but that shrinkage may begin sooner and at a lower temperature with increasing oxide content. This is a point that may have considerable practical importance.

Of the various other influences of oxygen content the most important, practically, are the effect on the green strength of the pressing and on the final mechanical properties of the finished sintered compact. It would be most desirable if Dr. Hoar and Mr. Butler could arrange to continue their work with the same powder and investigate these two points. It might prove that in a similar way the presence of oxide is not wholly deleterious. They might then review all the factors concerned and come to a conclusion what is the optimum all-round percentage of oxygen. The oxygen content has also a considerable influence upon the cost of manufacture. Atomized and electrolytic copper powders, as produced, generally contain oxygen to the extent of 0.1%. Powders subsequently gas dried or gas reduced may have contents of the order of 0.01%, but, of course, they are considerably dearer. Amounts substantially below this figure could only be obtained commercially at even higher costs. Subject to any views which the authors may hold upon the influence of oxide content upon green strength and mechanical properties, it would appear as a first approximation that an oxygen content of a commercially produced copper powder of between 0.1 and 0.2% is likely to be the most desirable.

The authors are right to stress the fact that their findings pertain only to an electrolytic copper powder manufactured in the manner described. For example, it would not be desirable to generalize and state that expansion during sintering is necessarily always caused by gases or by the production of steam. This might indeed be the case with copper powders prepared from oxide initially by reduction, where expansion is frequently known to occur at temperatures considerably higher than those cited and may, of course, be due to more deep-seated oxide content. On the other hand, compacts prepared from electrolytic silver powder show considerable expansions at quite low temperatures, whether heated in air or in a reducing atmosphere.

The AUTHORS (*in reply*): With regard to Mr. Chadwick's interesting remarks, it is true that the powder used in our work would not be suitable for use in commercial practice without the usual pretreatment given to such powders; but it is gratifying to note that its compacting properties are in fact rather similar to those of the finer-grade treated powder referred to in Mr. Chadwick's Table A.

It is most improbable that any adventitious lubricant was introduced into our die. It is likely that compacting difficulties were avoided by the adoption of a favourable height : diameter ratio in the compacts and by the use of a highly polished 13% chromium steel die. In the investigation of changes occurring in the complex process of sintering in the presence of oxide, additional complications such as are known to be caused by traces of lubricants would have been more undesirable than those possibly caused by non-lubricated pressing.

Many of our compacts were examined micrographically, with results in such close accord with those obtained by previous workers that it was not thought justifiable to publish photomicrographs.

The micrographs of Cook and Pugh show that recrystallization occurs in copper compacts below even 400° C., but there is little doubt that this leaves the particle surfaces virtually unaltered, as can be seen by comparing the particle structures in the green and sintered compacts,



FIG. A.—Electrodeposited Copper Powder. $\times 200$; transmitted light.
(Chadwick.)

Although most of the oxygen is removed by a 4-hr. treatment in hydrogen at 435°C ., a good deal may remain in the body of a compact at much higher temperatures provided that a sufficiently high rate of heating is employed; we consider that the reduction of this oxide may well occur in the manner described (p. 370), leading to a point of inflection on the dilation curve. The chemical bonding of gas, to be expected when this is carbon dioxide formed during sintering in carbon monoxide, is unlikely for water, and we prefer the proposed mechanism of *mechanical* enclosure for the case of sintering in hydrogen.

We agree with Dr. Jones that the influence of oxygen content on the green and sintered strengths of the compact is of great interest; although time did not permit such investigations in the present work, we found no qualitative indications that these properties are impaired by oxygen contents of up to 0.5%. It is fortunate that oxygen contents of 0.1–0.2% appear to be desirable, because in our experience it is almost impossible to maintain powders of less than 0.1% oxygen content except in rigorously oxygen-free atmospheres, owing to surface oxidation.

We also agree with Dr. Jones that expansions occurring during the heat-treatment of compacts are not always caused by enclosed or evolved gases, although the expansion of silver compacts, which he mentions, may perhaps be attributed to the thermal decomposition of silver oxide or the evolution of dissolved oxygen. We have, however, recently shown* that the very large expansions that occur during the early stages of the heat-treatment of copper-nickel compacts are probably caused by interdiffusion of the two components.

* J. M. Butler and T. P. Hoar, *J. Inst. Metals*, 1951–52, **80**, 207.

DISCUSSION ON THE PAPER BY MR. E. C. W. PERRYMAN : " STRESS-CORROSION OF MAGNESIUM ALLOYS."

(*J. Inst. Metals*, this vol., p. 621.)

DR. F. A. FOX,* F.I.M. (Member): This paper is a useful one in helping to put this rather obscure subject on a more quantitative basis and also in providing a tool for further study by the demonstration that test results with distilled water correlate well with practical experience.

That there is still a great deal of work to be done on the stress-corrosion of magnesium alloys is already made plain by the author. Since in our present state of imperfect knowledge the effects of many variables are far from clear, it might be helpful if the author could give a few more facts that might be relevant about his test materials. He points out that plastically deformed material is more susceptible to stress-corrosion than annealed material. Can he give information as to how his sheet was made? Had it been cold rolled? How had it been flattened? If it had been roller-levelled, was there much directionality? The possibility of directionality in the sheet reminds one that the test specimens are reported as being all stressed in their stronger (transverse) direction. Would it be expected that the results would differ greatly if they had been stressed in the weaker, longitudinal direction?

The practical conditions in which stress-corrosion may occur are likely to be those in which there is stress and *intermittent* exposure to corrosive media. Presumably, with the same degree of aeration of the corrosive medium itself, intermittent exposure is more destructive than the same "under-water" time of continuous exposure.

The fact that oxygen plays a part in the stress-corrosion process may influence the choice of the best protective film to be applied to magnesium alloys which are to be subject to stress-corrosion. It may be noted from Table VIII (p. 638) that worse lives were obtained, at any rate with one alloy, when the specimen was chromated than when not chromated; a similar tendency is evident in some ordinary stress-free corrosion testing, at least when material of normal (not low-iron) purity is concerned. The chromate film is, however, itself oxygen-bearing. Would the author care to speculate as to whether material, stress-corrosion tested in distilled water, would give a better result after a protective treatment by one of the fluoride processes, than if tested without protection?

The author is to be congratulated on his micrographs.

The AUTHOR (*in reply*): The magnesium-5% aluminium alloy which formed the basis of this work was hot rolled from slab down to 0.2 in. thick and then cold rolled to gauge, and finally annealed at 330° C. for 1 hr. I am not able to say how the sheets were flattened, though it is most likely that they were flattened by stretching. We did no tests to investigate the effect of directionality on the stress-corrosion properties, but providing that the structure is equi-axed, I see no reason why the stress-corrosion susceptibility should be very different in the longitudinal and transverse directions. Logan and

* Deputy Technical Manager, H. J. Enthoven and Sons, Ltd., London.

Hessing,* working with similar materials, did in a few cases find a small difference in the threshold stress for the two directions, but I think it rather doubtful whether this difference is significant. In view of my results on the effect of oxygen, I should expect intermittent immersion to be more destructive than total or partial immersion, but without knowing the exact mechanism of stress-corrosion cracking in magnesium-base alloys, I prefer not to speculate on the relative merits of fluoride and chromate films.

* H. L. Logan and H. Hessing, *J. Research Nat. Bur. Stand.*, 1950, **44**, 233.

DISCUSSION ON THE PAPER BY DR. P. C. L. PFEIL : "THE CONSTITUTION OF URANIUM-MOLYBDENUM ALLOYS."

(*J. Inst. Metals*, 1950, 77, 553.)

DR. A. U. SEYBOLT* and MR. R. K. MCKECHNIE* : There has been considerable interest among those who have done some work on the uranium-molybdenum phase diagram on the question of the stability of the γ solid solution in the region near 20 at.-% molybdenum. According to reports issued under the ægis of the Manhattan District and the Atomic Energy Commission in the United States, alloys in this concentration region have been shown as thermodynamically stable, at least down to 500° C. However, some experiments of our own have led us to question this finding, and the following experiment was performed in an attempt to answer this question unequivocally.

A uranium alloy containing 9.4 wt.-% (about 20 at.-%) molybdenum was cast in the form of a $\frac{1}{2}$ -in. dia. round. It was alternately solution-treated at 850° C. and swaged at 300° C. in order to obtain maximum molybdenum in the γ solid solution. As-cast alloys in this region tend to have a second phase (α uranium) precipitated in the grain boundaries; it was hoped that alternate solution-treatment and working would result in bringing the whole of the second phase into solution. This treatment did result in breakdown of the grain-boundary structure and spheroidization of the constituent particles, but failed to get all of it into solution (see Fig. A, Plate LXXIX).

The rod, now $\frac{1}{4}$ in. in dia., was rolled to a strip 0.020 in. thick and heated at 650° C. for 5 days. After this heat-treatment, it appeared that some new α phase had formed, as shown by microscopic examination and by X-ray diffraction. In neither case, however, was the presence of newly-formed α definite enough to be convincing. The same sample was then heat-treated for an additional 5 days at 450° C. This second treatment yielded the structure shown in Fig. B (Plate LXXIX), and the presence of a large amount of α -uranium was readily revealed microscopically using polarized light, and by X-ray diffraction. In addition, there was no longer any γ -uranium remaining in the sample, which now was a mixture of α and a distorted γ of tetragonal symmetry, denoted γ' . Dr. C. W. Tucker of this laboratory has submitted some discussion of this structure (see below).

Hence on the basis of both X-ray and microscopic evidence, γ -uranium containing about 20 at.-% molybdenum is not thermodynamically stable at temperatures below about 450°-650° C.

DR. C. W. TUCKER,* JR. : Examination by X-ray diffraction of the alloy described by Dr. A. U. Seybolt and Mr. R. K. McKechnie (see above) has given evidence of a direct nature that the single γ -phase region does not extend to room temperature, at least in the region of 20 at.-% molybdenum, as Dr. Pfeil's results would indicate.

This conclusion is based on X-ray examination of an alloy containing

* Knolls Atomic Power Laboratory, General Electric Co., Inc., Schenectady, N.Y., U.S.A.



FIG. A.—Structure of Uranium-9.4 wt.-% Molybdenum Alloy. Mostly γ solid solution plus some α . As electrolytically polished in H_3PO_4 solution. $\times 250$. (Seybolt and McKechnie.)



FIG. B.—Structure of Uranium-9.4 wt.-% Molybdenum Alloy after 5 days at 450° C. α plus distorted γ' . Polarized light. $\times 150$. (Seybolt and McKechnie.)

[To face p. 760.]

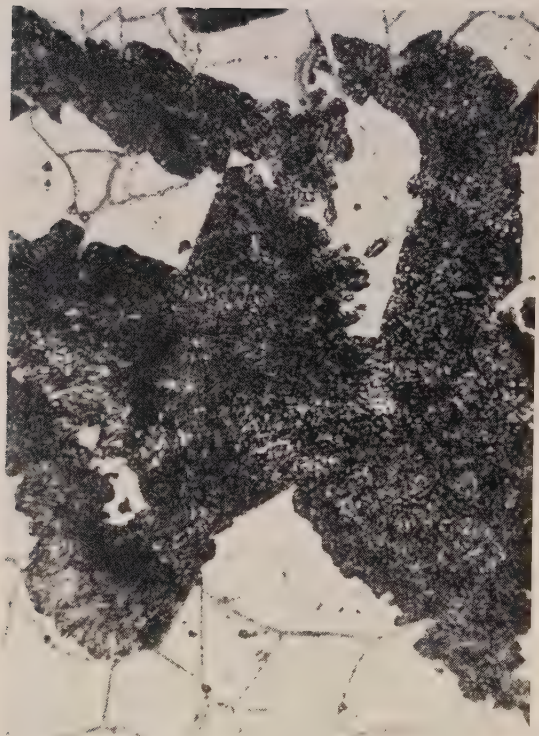


FIG. C.—Structure of Uranium-23 at.% Molybdenum Alloy, Annealed 2 weeks at 900° C., followed by 2 weeks at 500° C. γ' + finely divided mixture of α and γ' . Etched in 50% nitric, 50% acetic mixed acids. $\times 400$. (*Pfeil*).

9.4 wt.-% molybdenum after the treatment described by Dr. Seybolt and Mr. McKechnie. One sample was annealed for 5 days at 650° C. and another for 5 days at 450° C. Examined by X-ray diffraction, the sample annealed at 650° C. showed the γ phase with $a_0 = 3.399 \text{ \AA}$. From the data of Wilson and Rundle,* this corresponds to a composition of 9.68 wt.-% molybdenum, which agrees quite favourably with the chemical value of 9.37 %. In addition to the strong γ -phase lines, a few faint α -phase lines were observed.

The sample annealed at 450° C. showed, in addition to a strong α -phase pattern, a heavy pattern of another phase. When the lines of the extra phase were analysed, they were found to correspond to a body-centred tetragonal structure with the dimensions $a_0 = 3.420$, $c_0 = 3.278 \text{ \AA}$, $c/a = 0.959$. Assuming the space group D_{4h}^{17} , the intensities of adjacent lines are proportional (apart from the usual correction factors which are generally slow functions of the Bragg angle) to the multiplicity, p , of the reflection. Table A shows that

TABLE A.—Comparison of Observed and Calculated Line Position and Intensities in Body-Centred Tetragonal γ' Phase of Uranium-Molybdenum System.

hkl	Multiplicity, p	Observed Intensity	d , \AA . Observed	$1/d^2$, \AA^{-2}	
				Observed	Calculated †
110	4	s	2.440	0.1680	0.1710
101	8	vs	2.390	0.1751	0.1786
200	4	s	1.717	0.3392	0.3420
002	2	m	1.646	0.3690	0.3723
211	16	vs	1.390	0.5176	0.5205 m
112	8	m	1.347	0.5511	0.5433 w
220	4	mw	1.213	0.6796	0.6840
202	8	mw	1.184	0.7133	0.7142
310	8	s	1.080	0.8573	0.8550 mw
		(Slightly broad)			
301	8	—	—	—	0.8625
103	8	mw	1.041	0.9228	0.9231
222	8	m	0.972	1.0565	1.0562 vw
321	16	m	0.911	1.2044	1.2045 w
312	16	m	0.903	1.2277	1.2272
123	16	m	0.889	1.2645	1.2651
400	4	mw	0.854	1.3699	1.3679 vw
004	2	vw	0.819	1.4916	1.4890
411	16	s (broad)	0.804	1.5465	1.5465
330	4	—	—	—	1.5389
303	8	ms	0.790	1.6007	1.6070 vs

† Intensities included in this column are those of possible interfering α -phase reflections.

this gives satisfactory agreement with the observed intensities and also that the calculated and observed $1/d^2$ values are in satisfactory agreement. The intensities indicated after certain of the reflections in the " $1/d^2$ calculated" column are those of possible interfering α -phase reflections. Except for the very last reflection, the α -phase reflections do not cause any important difficulties in the analysis.

* A. S. Wilson and R. E. Rundle, *Acta Cryst.*, 1949, **2**, 126.

That interpretation of the second phase in terms of the body-centred tetragonal structure (which I have called the γ' structure) is the correct one, and that this is not a case of doubling of lines due to γ -phase crystals of two different compositions, is seen by comparing the intensities of the first four reflections, for example. Also, the (222) reflection would be split if one had two body-centred lattices of different compositions.

Experiments with different annealing times at 450° C. have shown no reaction detectable at 7 hr., detectable progress after 22 hr., essentially complete reaction after 52 hr., and no further change after 25 days. These results on the 450° C. sample show that the γ phase is not stable at this temperature, but has decomposed to form the α and γ' phases.

In connection with the discussion of Brillouin-zone structure of the α , β , and γ phases, I can contribute some information which I have calculated in connection with the crystal structure of the β phase recently reported.* For this phase there is a Brillouin-zone boundary which is quite close to being tangent (at some fifty points) to a sphere containing six states per atom. This zone is quite symmetrical and suggests very strongly that the β -phase structure is stabilized by the closeness of this zone boundary to the surface of the Fermi distribution for six valence electrons per uranium atom.

The AUTHOR (*in reply*): At the time the paper was written, it was believed that, with 20 at.-% molybdenum in solution, the γ phase was stable down to room temperature. The reasons for this belief were: (i) no transformations were detected in a 19.9 at.-% molybdenum alloy (by analysis) in thermal-analysis and dilatometer experiments using cooling rates of 0.5–2° C./min.; and (ii) a sample of the same alloy remained homogeneous and single-phase after a treatment that consisted of slow cooling from 600° to 425° C. in 10 hr., annealing overnight at 425° C., followed by slow cooling from 425° C. to room temperature the next day. The hardness and microstructure of this specimen were the same as those of specimens of identical composition annealed and quenched from temperatures in the range 600°–1000° C. Subsequent experience has shown that the experiments did not provide a sufficiently close approach to equilibrium.

A new series of alloys nominally containing 20.5–31 at.-% molybdenum have now been prepared by argon-arc melting. They were annealed for 1–2 weeks at 900°–1000° C. to eliminate the coring of the matrix. Very small amounts of a light-grey phase were visible under the microscope, but this constituent is attributed to a uranium oxide, carbide, or nitride rather than to α -uranium. After preliminary homogenization, several specimens were annealed at 500° C. for 14 days. The alloys containing 20.5 and 23 at.-% molybdenum showed a finely divided, rapid-etching two-phase structure present along the grain boundaries and in areas within the grains (see Fig. C, Plate LXXX). The two-phase structure was not found in the nominal 29 and 31 at.-% alloys annealed at 500° C., though after etching the grains showed surface unevenness. The 26 at.-% alloy has not been annealed at 500° C. except in the powdered condition.

Powders taken from a series of alloys homogenized at 900°–1000° C., have been annealed at 500° C. for 21 days. Diffraction patterns were taken in a 19-cm. camera with $\text{CuK}\alpha$ radiation. The 29 and 31 at.-% alloys gave diffraction lines approximately of the spacings listed by Tucker in Table A, but no α -uranium lines were visible. A few weak or very weak lines were also present, not attributable to any known uranium oxide, carbide, or nitride. In addition to this diffraction pattern, the 20.5 and 23 at.-% alloys showed lines due to α -uranium. These were much more intense in the 20.5 than in the 23 at.-%

* C. W. Tucker, Jr., *Acta Cryst.*, 1951, 4, 425.

alloy. A very weak diffraction pattern of α -uranium was shown by the 26 at.-% alloy. If (i) the actual compositions of the alloys correspond with the intended compositions; (ii) the loss of one or other constituent during annealing, particularly in the powder state, is negligible; and (iii) the annealing treatments at 500° C. have approached equilibrium conditions sufficiently well, then these results suggest that at 500° C. there is a phase boundary between 26 and 29 at.-% molybdenum.

The main lines of this set of diffraction patterns (other than those of α -uranium) could be indexed in terms of a body-centred tetragonal unit cell or an equivalent face-centred tetragonal cell. The patterns were of sufficiently high quality to resolve the (310) and the (301) lines. For the 31 at.-% specimen, the extrapolated lattice parameters referred to a body-centred tetragonal cell were $a = 3.423_6$, $c = 3.231_6$ Å., giving an axial ratio $c/a = 0.9535$.

A similar series of X-ray-diffraction patterns have also been obtained from previously homogenized alloys annealed in the powdered condition for periods up to 4 weeks at 450° C. The lines were not as sharp as those from the 500° C. series, but were otherwise similar. The 26 at.-% alloy showed a little more of the α -uranium pattern than it did after annealing at 500° C. The lattice parameters of the body-centred tetragonal phase in the 20.5 at.-% alloy were $a = 3.422$, $c = 3.276$ Å., to give an axial ratio of 0.957. Experiments on the annealing of a solid specimen of the 20.5 at.-% alloy at 450° C. revealed the precipitation of a finely divided two-phase structure, though the reaction was slower than that observed in the experiments at the Knolls Atomic Power Laboratory.

Taken in conjunction with the results of Seybolt and McKechnie and of Tucker, these experiments indicate that the γ body-centred cubic phase is not, in fact, stable down to room temperature in alloys containing 20–31 at.-% molybdenum, though it is suspected that what occurs is that the body-centred cubic phase becomes tetragonal as a result of ordering. Further work is in progress to test this possibility. At 500° C. α -uranium occurs in alloys containing more molybdenum than is indicated by Figs. 1 and 2 (pp. 559 and 563) of the paper; these figures therefore require amendment. Further annealing experiments are in progress at temperatures in the range 400°–650° C.

Dr. Tucker's calculations on the Brillouin-zone structure of β -uranium are of considerable interest. If β -uranium has 6 valence electrons per atom, on the assumption that the effective valency of molybdenum is also 6, it is difficult to explain on electronic grounds why the solubility of molybdenum in β -uranium is so restricted.

Since the paper was written, consideration of other alloy systems has suggested that the effective valency of γ -uranium may be 4 rather than 6. It may be possible to explain the fact that the lattice parameters of body-centred cubic uranium-molybdenum alloys approximately follow Vegard's law, as a result of the counteraction of two opposing factors: (i) increase of the electron: atom ratio by the addition of molybdenum, tending to increase the lattice dimensions; and (ii) attraction of molybdenum and uranium atoms to one another, tending to contract the lattice. If the interpretation of the body-centred tetragonal phase as an ordered form of the body-centred cubic phase is correct, ordering can be understood as a consequence of the attraction of uranium and molybdenum atoms.

The author wishes to thank the Director of the Atomic Energy Research Establishment for permission to publish this reply, and Mr. J. D. Browne for valuable assistance in measuring and evaluating the diffraction patterns.

OBITUARY.

HARRY DAVIES.

Mr. Harry Davies, Technical Manager at the Landore Works, Swansea, of Imperial Chemical Industries, Ltd., Metals Division, since 1934, died on 9 April 1951, aged 58, after a long illness.

He was a native of Stourbridge, Worcestershire, and was educated at the King Edward VI Grammar School; on leaving school he was for four years an articulated pupil to a Public Analyst, passing on to study metallurgy at Birmingham University (1911-15) where he gained a Bowen Research Scholarship. In 1915 he became Metallurgist with the Dunlop Rubber Co., Ltd., Birmingham, and in 1917 a Research Metallurgist with the Rudge-Whitworth Co., Ltd., Coventry and Birmingham. It was thus with a varied experience that he then entered the service of Elliott's Metal Co., Ltd., Selly Oak, in 1920 as Chemist and Metallurgist; this Company was eventually absorbed into Imperial Chemical Industries, Ltd., Metals Division.

Mr. Davies was intimately connected with general metallurgical affairs through the Institute (which he joined in 1916) and was from 1937 to 1939 and again from 1946 to 1948 Chairman of the South Wales Local Section. He was elected a Member of Council in 1950. He was a Vice-President of the Birmingham Metallurgical Society and a Fellow of the Institution of Metallurgists.

A specialist in metallography and an experienced teacher, Mr. Davies lectured on non-ferrous metals for some 18 years at the Technical College, Birmingham. He represented his Company in discussions in South Wales on technical education, and also in a similar capacity at a large symposium at Cardiff on Welsh resources in raw materials, power, and manpower.

Harry Davies was deeply interested in human aspects of industrial problems and devoted himself over many years to works councils, works safety, and works benevolent efforts. He took a very active part in the works social clubs in Birmingham and Swansea, and was for many years Chairman of the Landore Works Social Club. Highly regarded as a colleague and friend, he had both in and out of the non-ferrous industry a wide circle of friends who appreciated his quiet, steady, confident, but unselfish character, and it may truly be said that he lived respected and died regretted by all his many friends. He leaves a widow and one son.

G. H. ROGERS.

PIERRE-JOSEPH LEEMANS.

The death took place at Antwerp, Belgium, on 1 January 1951, of M. P. J. Leemans, Administrateur-Délégué de la Société Générale Métallurgique de Hoboken. M. Leemans, who combined an outstanding talent for organization with first-class ability as a technician, had devoted a great part of his energies to the building up of this important concern, and was one of the outstanding figures in the fields of non-ferrous metallurgy and of chemistry, both in Belgium and the Belgian Congo.

In recognition of his achievements, he was awarded in 1945 the André Dumont Prize of the Union des Ingénieurs sortis de l'Université de Louvain, where he himself had studied for his degree of Ingénieur civil des Mines.

M. Leemans had been a member of the Institute of Metals since 1924.

ARTHUR HOLLEY MUNDEY.

The death occurred on 5 July 1951, at the age of 83, of Mr. A. H. Munday, who was for many years a director of Fry's Metal Foundries, Ltd.

Mr. Munday began his career at the Royal Ordnance Factory, Woolwich, where he ultimately became chief metallurgist in the production department. At this period he was also a part-time lecturer at Northampton Polytechnic, London, and it was there that he first came into contact with Mr. J. H. Fry, who subsequently founded Fry's Metal Foundries. Mr. Munday left Woolwich to join this firm, and when it was made into a private company he became one of the directors. Later he was also on the boards of Fry's Diecastings, Ltd., and The Atlas Metals and Alloys Co., Ltd.

Mr. Munday played an important part in establishing the scientific basis of the manufacture and use of type metals and white metals. He published a considerable number of papers and articles, some of them in the Institute's *Journal*, and he was the author of a book "Tin and the Tin Industry".

Over a period of many years Mr. Munday took an active part in the affairs of the Institute, which he joined in 1918. He was Chairman of the London Local Section in 1927-28 and served as an ordinary Member of Council from 1930 to 1938. During the twenties and early thirties he was a frequent contributor to discussions at Institute meetings. He was closely associated with the formation of the Printing and Allied Trades Research Association in 1936, and became first chairman of its Research Committee.

Mr. Munday had numerous interests outside his scientific work, and during the last war he played a prominent part in the A.R.P. organization of the district where he lived in south-east London. He was lately Chairman of the Board of Governors of King's Warren School, Plumstead, and was still a member of the Board at the time of his death.

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